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Studies in Photographic Sensitivity, Part I. The Effect of Heat on the Sensitivity Curve of Photographic Plates

By

Osamu Masaki

(Received October 29, 1928)

Abstract

In my paper entitled "Sensitizing Action of Heat on Photographic Plates for Infra-Red Ray,"[1] it was observed that previous heating of a photographic plate sensitizes the plate more for infra-red rays than for violet ones. The present experiments were carried out to find at various wave lengths the amount of sensitization called forth by a previous heating. The following facts were established from experiments carried out with twelve kinds of plates: (1) The contrasts always become steeper for all wave lengths. (2) The inertia of panchromatic plates and other slow plates was decreased, but that of high speed plates was increased. (3) In the former case, the amount of sensitization was greater in the red side of the maximum point of the sensitivity curve than in the violet side, while in the latter case the amount of desensitization was greater in the violet side, and was smaller in the other side. These facts mean that the maximum point in the sensitivity curve always shifts a little towards the red when the plate has been previously heated.

Introduction

In my paper entitled "Sensitizing Action of Heat on Photographic Plates for Infra-Red Ray," it was found that a previous heating of dry plates sensitizes the plate more for infra-red rays than ultra-violet ones. Afterwards, Kellner[2] found that heat did not influence selectively the action of lights of special wave lengths.

1 Jap. Jour. of Phys. **11**, 163 (1923)
2 Zeits. Wiss. Phot. **24**, 63 (1926)

In the present experiments, it was attempted by a more quantitative measurement to examine how the previous heating affects the forms of the characteristic curves corresponding to various wave lengths.

Apparatus and Method of the Experiment

The special plate holder employed in the previous investigation[1] was also used in these experiments. A constant-deviation spectrograph was adopted instead of a grating spectrograph to eliminate the superposition of the second order spectrum and a diffuse light. A small sector wheel was made in our work shop with special care, and it was tested by the method described in the following paragraph. This was placed in front of the slit of the spectograph and was rotated by a motor. This sector, as shown in Fig. 1, has a similar construction to Hurter and Driffield's disc, but instead of its stepped aperture this has two windows of continuously decreasing aperture which was reduced to one half as the radius was increased by one mm.. It was difficult to cut exactly apertures of such dimensions in a brass plate, and so it was constructed by combining two thin plates, one of which has two apertures with correct edges along ABC and A′B′C′ shown in Fig. 1 and the other with correct edges along ADC and A′D′C′.

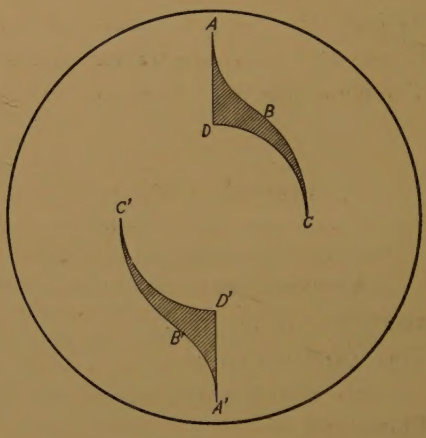

Fig. 1. The Sector.

As the light source, an incandescent lamp with a condensed filament was used, and this was first focussed by a lens on a small circular aperture, and the rays coming from this aperture were sent on to the sector after being made parallel by a photographic lens. For the sake of wave length scale the light from tin sparks was sent on to the slit of the spectrograph reflected by a right-angled prism placed temporarily in front of the sector.

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1 Loc. Cit.

The lamp current was supplied from a secondary battery which was used for this purpose only. The plate holder was heated to the required temperature in a steam bath before charging a dry plate. After this, both the plate holder and the plate were also kept at this temperature for one hour, and then an exposure was made with it.

All the plates to be investigated were cut out from a single plate and were developed simultaneously in a bath containing metol hydroquinone developer for 5 minutes. In the following experiments all the plates were developed in this way.

The densities of the negatives thus taken were measured by means of a Moll's microphotometer, the light deflected from the galvanometer being plotted on a section paper. A curve obtained by connecting these points represents the relation between the intensity of the light transmitted through the negative plate and log E. From these curves, density-log E curves, i. e. characteristic curves were obtained. The correction for a general fog was made according to the equation given by Wilsey.[1]

Testing of the Sector and the Method of Drawing Characteristic Curves

Although the sector was made with special care, the form of the aperture could not made correct and this error should be taken into account. The correction for this was made in the following way.

Six pieces were cut out from an Ilford Special Rapid Panchromatic Plate, and to each of them a series of exposures were given in the ratio of 2^0, 2^1, 2^2,.....2^5 by opening the shutter placed in front of the sector and timing with a stop watch. All the exposures were given 3 minutes after the lamp had been lighted, as the current flowing in the lamp required 3 minutes to reach its steady state. In order to prevent the errors due to the fatigue of the battery a similar series of exposures were given in a reverse order to another six pieces cut out from another dry plate, and the resultant values of the two series were averaged. The plates thus treated were measured by the microphotometer. Fig. 2, B represents a series of such curves. Curve I shows one corresponding to a 1 minute exposure, curve II, 2 min. exposure, etc.. The horizontal distances of any two adjoining curves must always be equal if the sector has been made correctly but generally this was not the case. The error

1 Eastman Kodak Co. Research Lab. Commu. No. 246. Photo. J. **65**. 454 (1925)

due to such incorrectness in the sector was eliminated by the following method :—

A line parallel to the abscissa was drawn from the point a, where the curve I intersects the ordinate corresponding to the maximum exposure, and the points where this line intersected curves II, III,.....lettered a_2, a_3,..... . From a_2, a straight line was drawn parallel to the ordinate and its intersection with the curve I lettered b_1 ; from b_1 a line was drawn parallel to a_1 a_2 and its intersections with the curve II, III,..... lettered b_2, b_3,..... . From b_2 a line was drawn parallel to the ordinate and its intersection with curve I lettered c_1. This process being extended to the curve VI, two systems of cross lines, one being vertical and the other being horizontal were obtained as shown in Fig. 2, B.

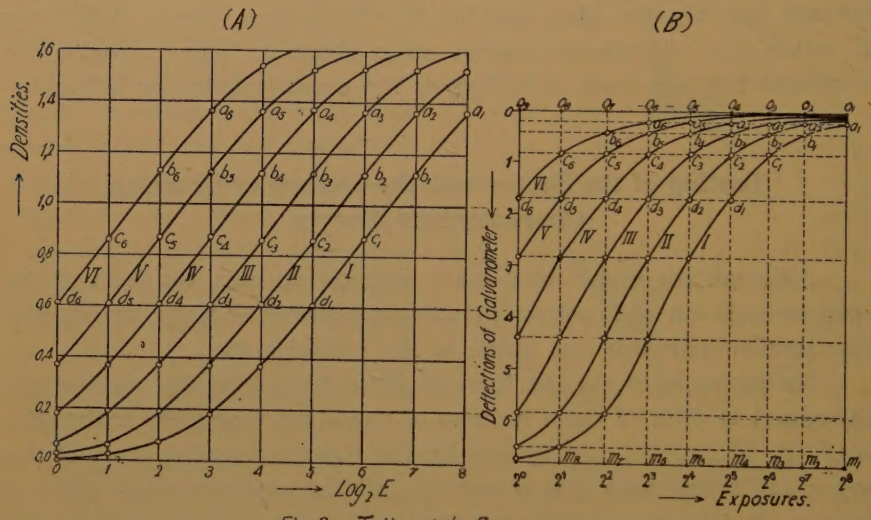

Fig. 2. Testing of the Sector.

If the sector be correctly made the distances between every two adjoining lines parallel to the ordinate must be equal, but in the present case the distances between these lines were not perfectly equal. But in the computation of densities if we use these vertical lines as the ordinates corresponding to the exposures 2^0, 2^1, 2^2.....2^8, the error due to the incorrectness of the sector-aperture may be eliminated. All the characteristic curves given in the following paragraphs were drawn in this way. An example of obtaining a characteristic curve is given here. Let the line o_1o_2..... represent the line of zero deflection of the galvanometer and the line m_1m_2..... be the one of the maximum

deflextion, corresponding to an unexposed portion of the plate. Then $\log_{10}(o_2m_2/o_2a_2)$ represents the density of the point a_2, and thus the curves in Fig. 2, A were obtained which represent D-log E diagram i. e. characteristic curves of the plate corresponding to the curves in Fig. 2, B. As seen from the figure all the curves now become parallel and similar in their forms, and are separated by the same distance from one another.

Effects of Heat on the Form of Characteristic Curves for Rays of Various Wave Lengths

Three pieces were cut out from one plate, and to one of these the exposure to the sector spectrum was given at room temperature (15°C.). Next, the plate holder only was heated up to 80°C. in a steam bath, and when its temperature reached the above value the second piece of the plate was placed in it and this was again kept in the bath until the thermometer inserted into the plate holder reached 80° C.. Then the same exposure as the first one was given to this.

Finally, after the plate holder had cooled down to the room temperature, the same was repeated with the third piece of the plate. Figs. A and B in Plate I show the photographs taken in the first and second ways for Wratten and Wainwright Process Panchromatic Plates, and Figs. C and D are the similar photographs for Ilford Process Panchromatic Plates. Characteristic curves of thus treated and untreated plates for rays of the wave lengths of 450, 500, 550, 600, 650, and 700 $\mu\mu$. are given in Fig. 3 from which the sensitivity curves were drawn as shown in Fig. 4, A, the ordinate of this diagram representing the value of log i, where i is the inertia of the plate.

Now let us define the amount of sensitization due to preliminary heating by $\Delta \log i = \log i - \log i'$, where i′ is the inertia of the treated plate and i is that of the untreated one. Then the so-called sensitizing curve is drawn with a dashed line taking wave length horizontally and log i vertically as shown in Fig. 4, A. The changes of gamma of characteristic curves for the rays of various wave lengths are represented by a dotted line in the same figure. Fig. 4, B, C, and D also represent the diagrams corresponding to Fig. 4, A for other panchromatic plates. In all these plates, heat always sensitizes the plate for all spectral regions although the form of the sensitizing curve depends upon the nature of plates. The curves for plates having many maxima and minima in their sensitivity curves are very complex. But generally the sensitizing action

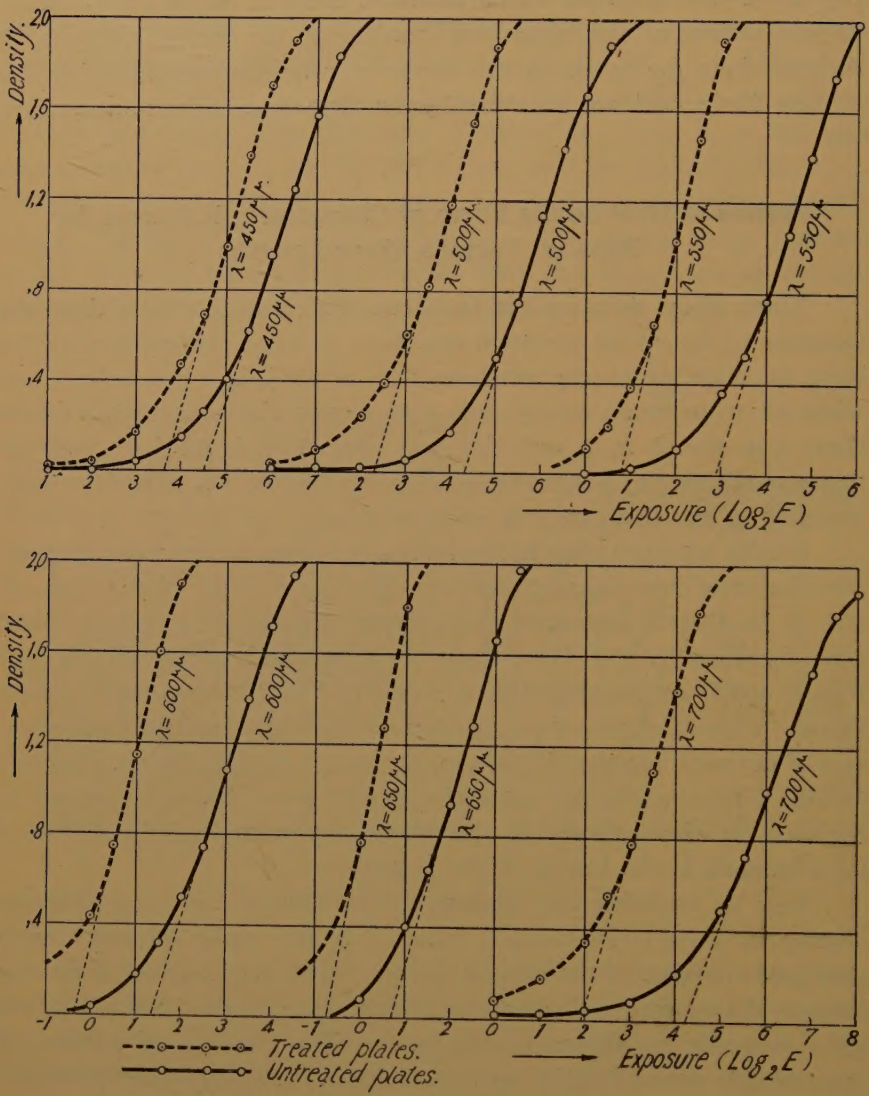

Fig. 3. Effects of Heat on the Characteristic Curves.

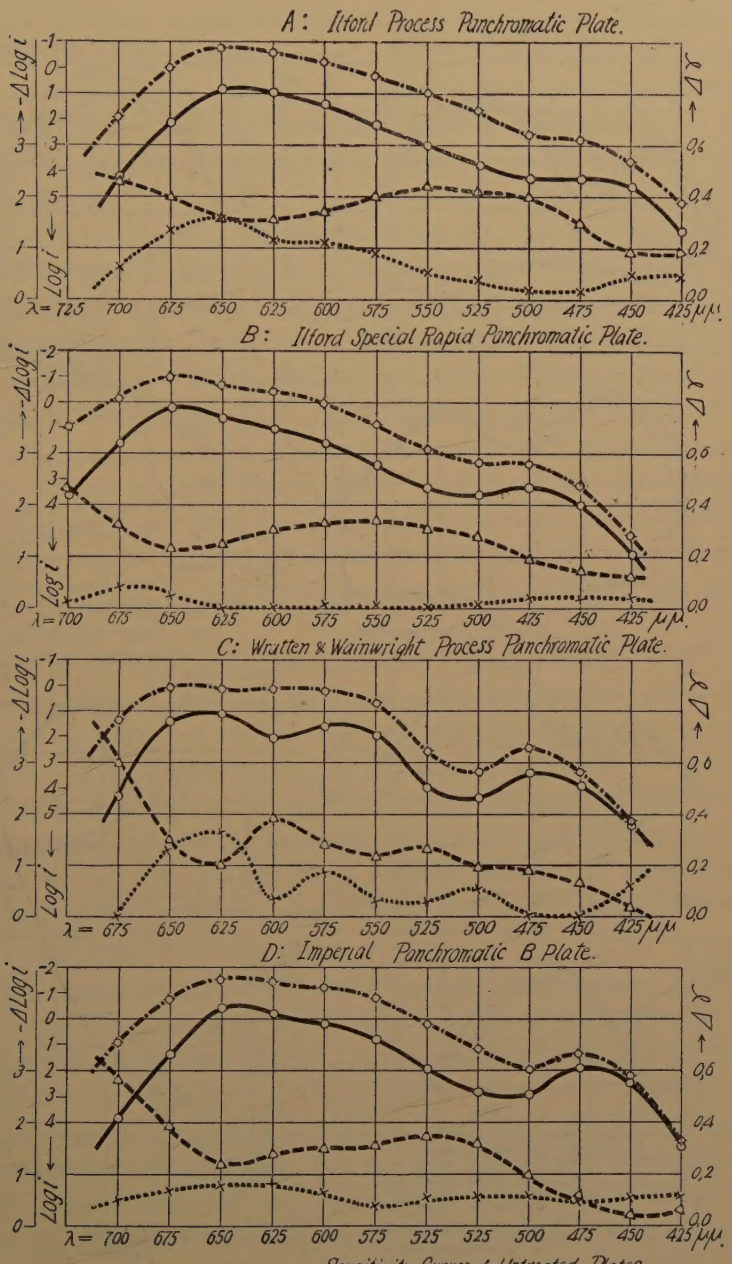
A: Ilford Process Panchromatic Plate.
B: Ilford Special Rapid Panchromatic Plate.
C: Wratten & Wainwright Process Panchromatic Plate.
D: Imperial Panchromatic B Plate.
-Δ Log i
Log i
Δγ
λ = 725 700 675 650 625 600 575 550 525 500 475 450 425 μμ
λ = 700 675 650 625 600 575 550 525 500 475 450 425 μμ
λ = 675 650 625 600 575 550 525 500 475 450 425 μμ
Sensitivity Curves of Untreated Plates.
" " Treated Plates.
Sensitizing Curves (Δ Log i).
Changes of Contrasts (Δγ).

Fig. 4. Effects of Heat on the Sensitivity Curves of Panchromatic Plates.

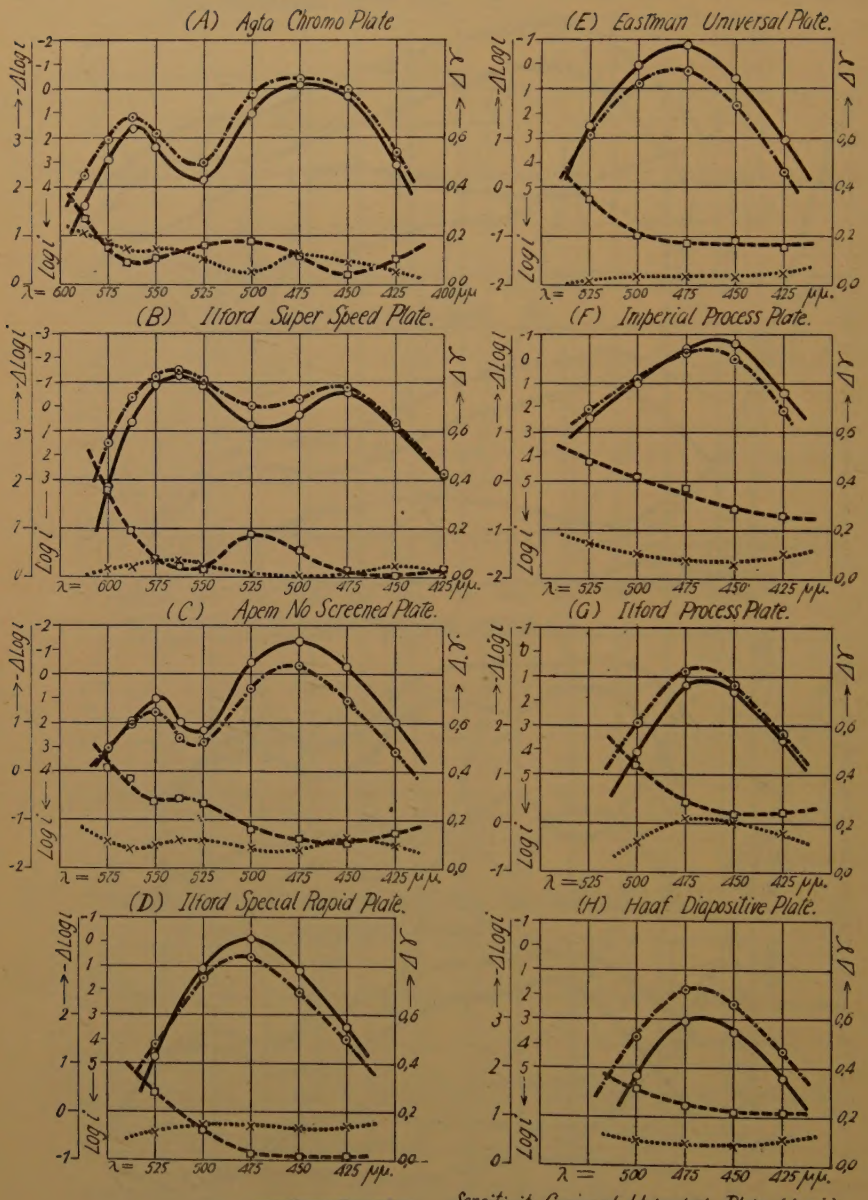
(A) Agfa Chromo Plate
(E) Eastman Universal Plate.
(B) Ilford Super Speed Plate.
(F) Imperial Process Plate.
(C) Apem No Screened Plate.
(G) Ilford Process Plate.
(D) Ilford Special Rapid Plate.
(H) Haaf Diapositive Plate.
-Δ Log i
Log i'
Δ γ
λ = 600 575 550 525 500 475 450 425 400 μμ
λ = 525 500 475 450 425 μμ
Sensitivity Curves of Untreated Plates. (Log i).
" Treated Plates. (Log i').
Sensitizing Curves. (Δ Log i).
Changes of Contrasts. (Δ γ).

Fig. 5. Effects of Heat on the Sensitivity Curves of Orthochromatic and Ordinary Plates.

is smaller for more refrangible rays and greater for less refrangible rays, i. e., more precisely, the sensitizing action is usually greater in the red side of each maximum point of the sensitive curves than in its violet side.

Fig. 5, A to C also represent the diagrams corresponding to Fig. 4 for some orthochromatic plates, and Fig. 5, D to H those for various ordinary plates.

From these results, it was observed that there are two distinct effects produced by heating plates; one of which is the decrease of the inertia, while the other is increase of it. The inertia of panchromatic and other slow plates is reduced, but that of high speed plates is increased by the preliminary heating. Plates such as the Eastman Universal Plate and the Ilford Super Speed Plate (700° H. D.) are examples of the latter. But even in the cases where heat reduces the sensitivity of the plate, the amount of desensitization is greater in the shorter wave length side of the maximum point of the sensitivity curve and is smaller in its longer wave length side; moreover, in some plates heat sensitizes the plate for less refrangible rays. This is seen in the Ilford Special Rapid Plate and the Imperial Process Plate.

Thus in ordinary plates the sensitizing curve gradually rises towards long wave lengths giving no minimum point, whenever the effect of heat is positive or negative. When the plate has been originally sensitized with dyes as in panchromatic or orthochromatic plates, the sensitizing curve has a minimum point near the maximum point of the sensitivity curve, but the amount of sensitization is remarkably greater in all the cases in the red side of it. These results mean that the maximum point of the sensitivity curve is always shifted without exception towards the longer wave lengths by the action of heat.

The amount of this displacement is small, and is about 50 Å. for a raise of the temperature by 65° C. or 0.8 Å. per degree, therefore it will be difficult to detect this shifting on the negative plate unless adequate care is taken.

The change of contrast (γ) due to previous heating was generally opposite to that of sensitivity, that is, the greater the sensitization, the smaller is the increase of contrast, and the smaller the sensitization, the greater the change of contrast. Generally, the contrast was increased by heating for all kinds of plates and in panchromatic and orthochromatic plates the change of contrast was greater for the rays of long wave lengths, but in ordinary plates this change of contrast was small, and did not seem to be selective to certain wave lengths.

Wallace[1] found that at higher temperatures photographic plates have smaller sensitivity and greater contrast than at lower temperatures indicating that the characteristic curves in the two cases intersect at some point. But in the light of the present experiments it has been ascertained that his statement is correct only for ordinary high speed plates for the rays of short wave length, but not for panchromatic and slow plates.

Life of Plates Sensitized by Heat

The sensitizing action of heat on photographic plate was not reduced immediately to nothing as the temperature fell, but was kept for serveral hours after the plate reached the room temperature. Fig. 6 represents this relation. At the end of the first one hour, it was reduced to $2/3$ of the maximum value, after that time the rate of its reduction became very small and approached asymptotically to zero. For the less refrangible rays this effect was kept for a longer time than for the more refrangible rays.

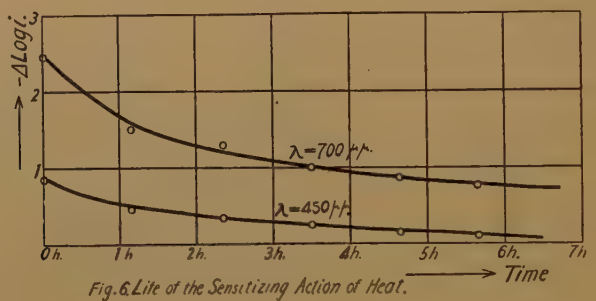

Fig. 6. Life of the Sensitizing Action of Heat.

The Effect of Drying

It is imposible to distinguish the effect of heat from the drying effect that accompanies the raising of the plate temperature. Although the greatest precautions were taken to keep the plates in a dry condition by keeping them in a desiccator, the results of the above experiments may not be free from the objection that the effect of drying the plates enters into them. But in our country the humidity is rather small in autumn and winter, during which seasons the present experiments were carried out. The effect of the latter, if it exists, would therefore be very small.

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1 Astro. Phys. J. **28**, 39 (1908)

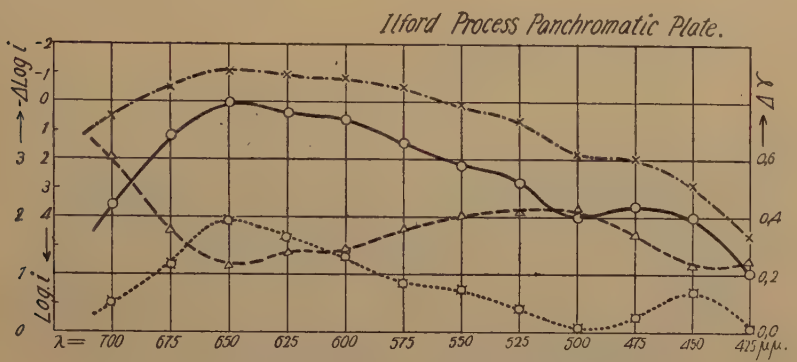


Fig. 7 Effect of Heat on a Perfectly Dried Plate.

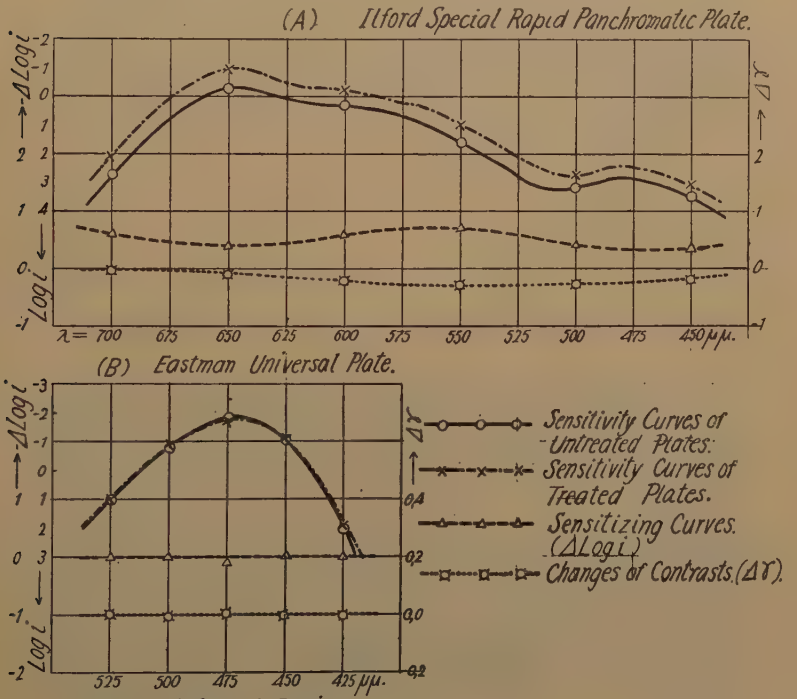

(A) Ilford Special Rapid Panchromatic Plate.
-Δ Log i
Log i
Δγ
λ= 700 675 650 625 600 575 550 525 500 475 450 μμ.
(B) Eastman Universal Plate.
-Δ Log i
Log i
Δγ
525 500 475 450 425 μμ.
Sensitivity Curves of Untreated Plates.
Sensitivity Curves of Treated Plates.
Sensitizing Curves. (Δ Log i)
Changes of Contrasts. (Δγ).

Fig. 8. Effect of Drying.

In order to ascertain this, however, similar experiments to the above were carried out with specially well dried plates. The plates were put film-side downward in a porcelain vessel containing phosphorus pentoxide, and the whole vessel was again kept in a desiccator containing calcium chloride for a few days. On one half of the plate the exposure was given

by the above method without heating it, and on the other half the exposure was given after heating.

The result of this experiment will be seen from the curves given in Fig. 7, which is quite similar to the one given in Fig. 4. It may be said from this fact that the effects of heat described in the previous paragraph are probably due to heating the plate only. Moreover in order to obtain only the effect of drying, similar exposures were given to two plates, one of which had been kept in ordinary air while the other had been well dried in the desiccator used in the above experiment. The results obtained with Ilford Special Rapid Panchromatic and Eastman Universal Plates are given in Fig. 8; A and B.

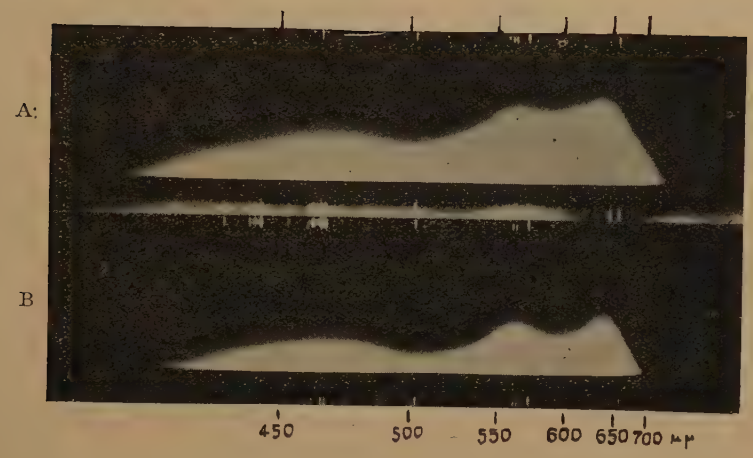
Comparing the above two experiments we may conclude that the effect of drying is not analogous to that of heating. The sensitizing action of drying was generally very much smaller than that of heating and had not much difference in the two sides of the maximum point in the sensitivity curve. Consequently by the process of drying, the spectral sensitivity of photographic plates can not be extended towards the infra-red region. Particularly, in ordinary high speed plates, heat reduced their sensitivity greatly in the violet region and slightly in the red region, but the drying had no such effect.

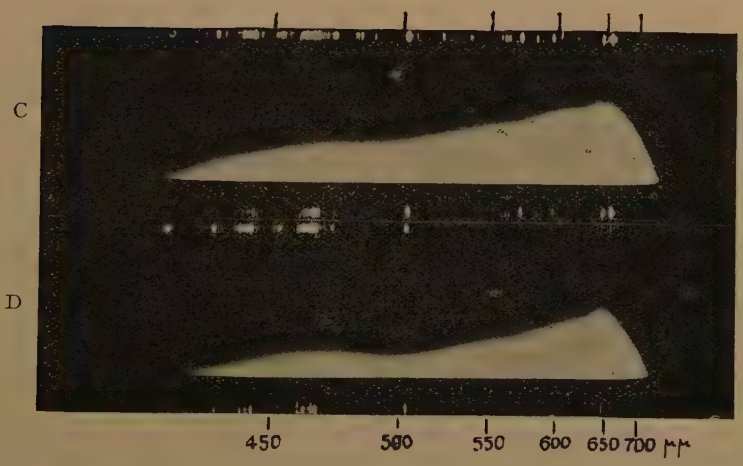
The result obtained in the present experiments seem more favourable to the photoelectric conductivity theory of latent images than the photoelectric theory.

An experiment is now going on to see how the photoelectric conductivity of silver bromide produced by rays of various wave lengths depends on its temperature.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Kimura for his valuable advice and the great interest he has taken in this investigation, and the author's thanks are also due to President T. Maruyama of the Konan College for his kind offices.

Plate I





Studies in Photographic Sensitivity, Part II. On the Sensitivity of Photographic Plates at Various Temperatures

By

Osamu Masaki

(Received October 29, 1928)

Abstract

By raising the temperature of photographic plates the sensitivity of panchromatic and other slow emulsion plates was found to increase while that of rapid plates was found to behave in the opposite way. But their contrasts became always steeper. The corresponding change in the inertia of characteristic curves was slower up to the temperature of about 30°C. and then became greater as the temperature was raised to about 70°C. and again became slower at higher temperatures. The change in the contrast was smaller up to the temperature of about 60°C. and became more marked at higher temperatures. γ was found to be proportional to e^{t^2}, t being the temperature of the plate in °C. The tangents at inflexion points of the characteristic curves taken at various temperatures seem to meet at one point. From these facts the following formula expressing the density as a function of temperature is obtained

$$D = D_m e^{at^2}\left\{1 - e^{-(bt+c)E}\right\},$$

where a, b, and c are constants and D_m is the maximum density at 0°C. This formula is valid from 10°C. up to 80°C.

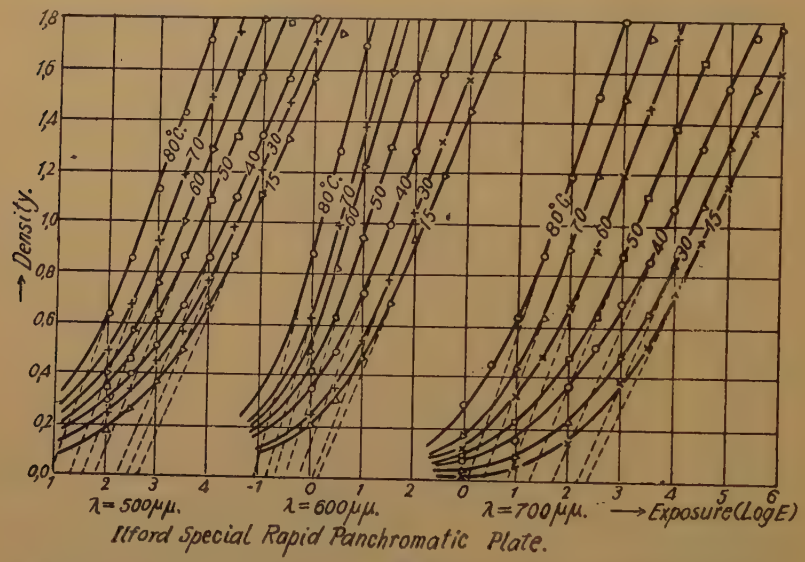
Experiments

In my first paper[1] it was shown that by raising the temperature of photographic plates the contrasts of their characteristic curves always become steeper and the sensitivity of such plates as panchromatic and those of slow emulsion is increased, but that of such plates as very rapid emulsion is decreased. In the present experiment it is intended

1 These Memoirs **12**, 1, (1928)

to find how the inertia and contrast γ of the plate depend on its tempeature.

The experimental apparatus and methods were the same as those given in previous paper. Several pieces were cut out from a plate carefully preserved in a desiccator, and they were heated before the exposure at a desired temperature for one hour in a steam bath. The



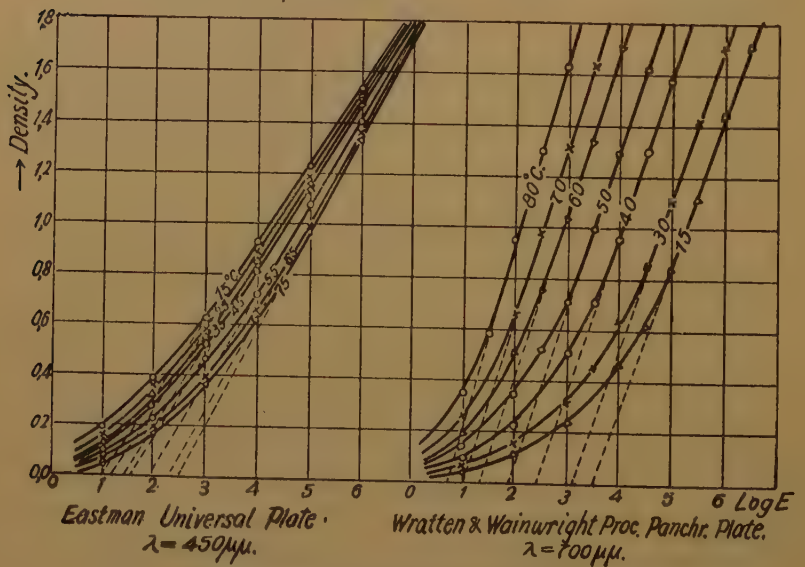


Fig. 1. Characteristic Curves taken at Various Temperatures.

temperature was read by a thermometer inserted into the plate holder, the temperature being kept as constant as possible during the exposure, but it varied within $\pm 1°C$.

Analysis of the Characteristic Curves

The characteristic curves of certain photographic plates taken at various temperatures for lights of special wave lengths are represented in fig. 1. From these curves the inertia and the contrast of such plates are plotted against the temperatures as shown in Fig. 2.

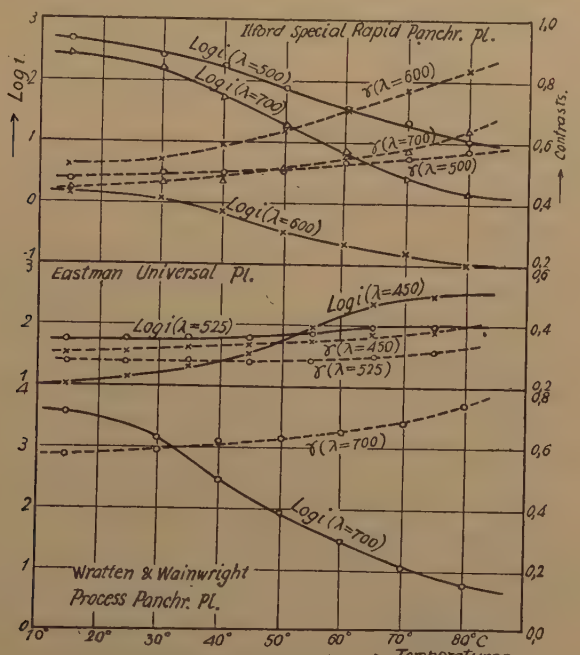


Fig. 2. Dependency of Sensitivities and Contrasts on the Temperature.

The values of inertia log i and contrast γ determined from the characteristic curves are given in the following tables.

As is seen from the diagrams, though the variation of the inertia is generally slow up to the temperature of about 30°C., it becomes very marked after that temperature is reached and again becomes smaller at temperatures higher than 70°C.. On the other hand, the increasing of the contrast is not marked at lower temperatures until the temperature of 50°C. or 60°C. is reached, but becomes gradually steeper at higher

Table I

t	Ilford Special Rapid Panchromatic Plate.					
	λ=500 μμ.		λ=600 μμ.		λ=700 μμ.	
	Log i	γ	Log i	γ	Log i	γ
15°C.	2.65	0.466	2.17	0.520	2.40	0.440
30°C.	2.48	0.482	2.06	0.536	2.20	0.462
40°C.	2.25	0.488	1.82	0.590	1.70	0.468
50°C.	1.85	0.510	1.50	0.636	1.28	0.508
60°C.	1.53	0.524	1.30	0.700	0.86	0.554
70°C.	1.32	0.550	1.20	0.770	0.39	0.562
80°C.	0.97	0.566	0.96	0.840	0.14	0.634

t	Wratten & Wainwright Process Panchr. Pl.		t	Eastman Universal Plate.			
	λ=700 μμ.			λ=450 μμ.		λ=525 μμ.	
	Log i	γ		Log i	γ	Log i	γ
15°C.	3.54	0.575	15°C.	1.00	0.304	1.76	0.270
30°C.	3.13	0.588	25°C.	1.16	0.306	1.75	0.270
40°C.	2.45	0.613	35°C.	1.40	0.328	1.79	0.280
50°C.	1.90	0.618	45°C.	1.54	0.332	1.76	0.274
60°C.	1.45	0.645	55°C.	1.94	0.346	1.84	0.286
70°C.	1.06	0.675	65°C.	2.37	0.374	1.95	0.296
80°C.	0.78	0.740	75°C.	2.44	0.376	1.95	0.310

temperatures. It may be assumed from the curves that the contrast changes exponentially with the temperature.

Now if we plot the values of $\log \gamma$ against t^2, the straight lines shown in Fig. 4 are obtained. Thus the contrast γ is represented by the expression:

$$\gamma = e^{at^2+k} \quad \text{.....(1),}$$

where a and k are constants depending on the wave length of the light used for the exposure, the time of the development and the properties of the emulsion, and t is the temperature expressed in °C..

The constants a and k of the equation (1) are calculated from the

straight lines given in Fig. 4 as follows;—

Table II

	Ilford Spec. Rap. Panchr. Pl.		Eastman Universal Pl.
	λ=500 μμ.	λ=700 μμ.	λ=450 μμ.
a	0.0000300	0.000057	0.000044
k	−0.74	−0.822	−1.172

It may also be seen that the tangents at the point of inflexion of each characteristic curve given in Fig. 1 seem to meet at one point. If this is correct for every temperature the following relation must hold:

$$\frac{-\beta}{\log_2 i - \alpha} = \gamma \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where α and β are the coordinates of the point of intersection.

That is, there must be linear relation between $\frac{1}{\gamma}$ and $\log_2 i$.

A graph is therefore drawn taking $1/\gamma$ as abscissa and $\log i$ as ordinate and a straight line is thus also obtained. The examples of such diagrams are represented in Fig. 3, in which points almost lie on the straight lines showing that equation (2) holds in the present case, *i. e.*, the tangents at the point of inflexion to each characteristic curve taken at various temperatures intersect at a point.

The constants α, β are calculated from these lines as follows.

Table III

	Ilford Spec. Rap. Panchr. Pl.		Eastman Universal Pl.
	λ=500 μμ.	λ=700 μμ.	λ=450 μμ.
α	−8.5	−6.0	2.4
β	−5.3	−3.8	8.8

Empirical Formula

The equation connecting the relation between the density of a developed photographic plate and the exposure is given by the following equation by Elder,

$$D = D_m (1 - e^{-KE}), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3),$$

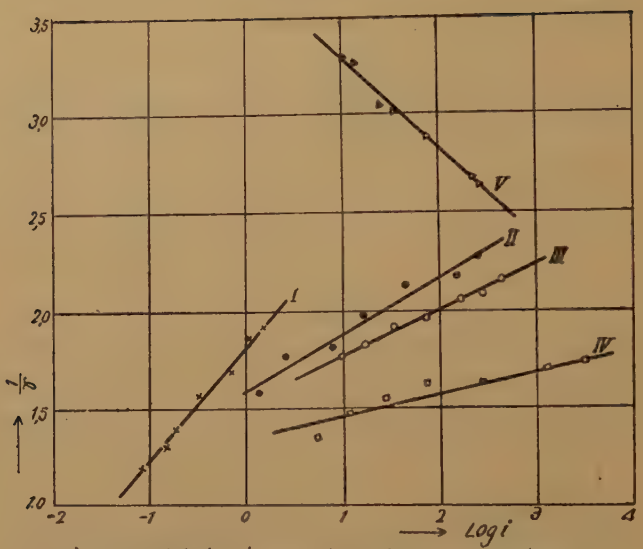


Fig. 3. The Relations between the Inertias and the Contrasts.

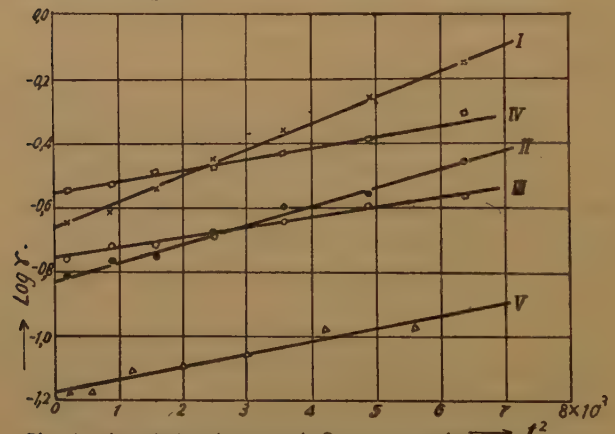


Fig. 4. The Relations between the Contrasts and the Temperatures.

I Ilford Special Rapid Panchr. pl. (λ=600 $\mu\mu$.)
II " " " (λ=700 $\mu\mu$.)
III " " " (λ=500 $\mu\mu$.)
IV Wratten & Wainwright Process Panchr. Pl. (λ=700 $\mu\mu$.)
V Eastman Universal Plate. (λ=450 $\mu\mu$.)

temperature of the plate being supposed to be constant. But if the temperature of the dry plate is changed, D_m and K should also vary as a certain function of the temperature, consequently, in considering characteristic curves, $x=\log E$ is to be taken as abscissa, and then we get

$$D=D_m(t)\left\{1-e^{-K(t)e^x}\right\} \quad \text{.....(4),}$$

by differentiating this equation we obtain

$$\frac{dD}{dx}=D_m(t)K(t)e^{x-K(t)e^x} \quad \text{.....(5)},$$

$$\frac{d^2D}{dx^2}=D_m(t)e^{x-K(t)e^x}\{1-K(t)e^x\}.$$

At the inflexion point this equatin must be equal to zero, or

$$1-K(t)e^x=0$$

this is,

$$K(t)=e^{-x} \quad \text{.....(6)}.$$

Substituting the last value in equation (5) we obtain

$$\frac{dD}{dx}=D_m(t)e^{-1}$$

This is the slope of the tangent at the inflexion point of the characteristic curve, and it is not anything else than the contrast of the characteristic curve. But in an ordinary characteristic curve $E=2^\xi$ is taken as the exposure inteat of $E=e^x$, thus the abscissa axis in the accompanying curves representing the value of ξ, consequently, $2^\xi=e^x$ or $\xi \log 2=x$

then

$$\frac{d\xi}{dx}=\frac{1}{\log 2}$$

therefore

$$\frac{dD}{dx}=\frac{dD}{d\xi}\frac{d\xi}{dx}=\frac{dD}{d\xi}\frac{1}{\log 2}$$

$$\frac{dD}{d\xi}=D_m(t)\log 2\cdot e^{-1}$$

that is

$$\gamma=D_m(t)e^{-1.366} \quad \text{.....(7)},$$

because $\text{Log } 2=e^{-0.366}$.

As shown above the contrast may be given by the equation

$$\gamma=e^{at^2+k}$$

therefore

$$D_m(t)e^{-1.366}=e^{at^2+k}$$

or

$$D_m(t)=e.^{at^2+k+1.366}$$

putting

$$k+1.366=k'$$

$$D_m(t)=e^{at^2}+k' \quad \text{.....(8)}$$

The last equation shows how the maximum density changes with the temperature. Now, let the value of $D_m(t)$ when $t=0$ be represented by D_m, then $D_m=e^{k'}$, and equation (4) becomes

$$D=D_m e^{at^2}\{1-e^{-K(t)E}\} \quad \text{.....(9)}$$

In order to see how the relation (8) holds in the present experiment, densities calculated from equation (8) and those calculated from observed characteristic curve are compared in the following table, in which the data are taken from Ilford Special Rapid Panchlomatic Plates for the ray of $\lambda=500\ \mu\mu$..

Table IV

Temp.	15°C.	30°C.	40°C.	50°C.	60°C.	70°C.	80°C.
D_m cal. from (8).	1.90	1.94	1.98	2.04	2.10	2.18	2.29
D_m cal. from real curve.	1.93	1.97	2.02	2.04	2.13	2.18	2.25
Difference.	0.03	0.03	0.04	0.00	0.03	0.00	−0.04

The maximum densities given in the above table are calculated according to a method similar to that given by Nietz in his book " Theory of development " on p. 89. Thus it will be observed that our equation (9) gives correct results as the differences lie within the limits of experimental errors.

Next, the functional form of $K(t)$ in the equation (9) must be determined. The equation (9) is now transformed into the following form :

$$\mathrm{Log}\frac{D_m e^{at^2}}{D_m e^{at^2}-D}=K(t)E \quad \text{.....(10).}$$

Thus, the value of the left hand side of the equation (10) is proportional to $K(t)$ when the exposure is constant. If we draw curves representing $\mathrm{Log}\ D_m e^{at^2}/(D_m e^{at^2}-D)$ as a function of $K(t)$, a straight line is obtained only when t^2 is taken as abscissa.

Fig. 5 represents such relations for some kinds of plates for several values of E.

Therefore the function $K(t)$ is to be expressed as follows

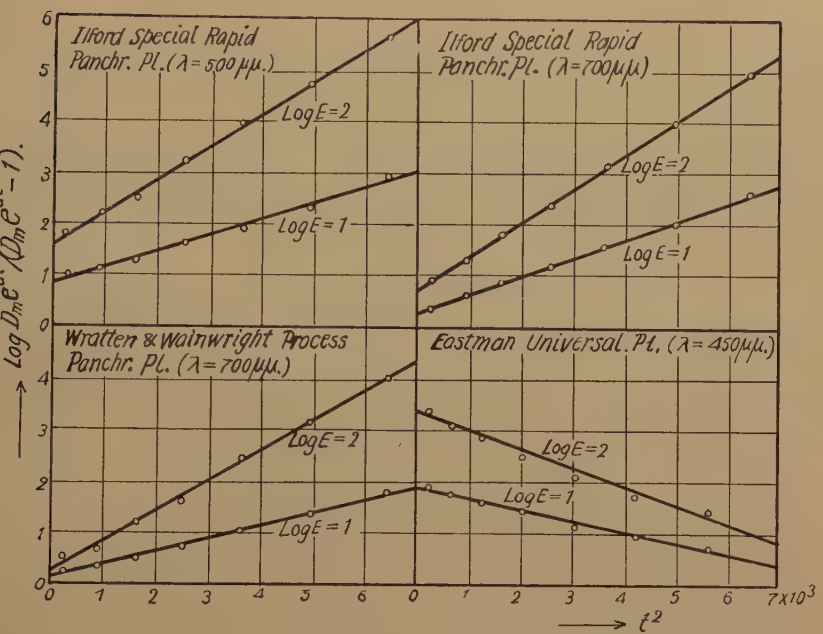


Fig. 5.

$$K(t)=bt^2+c \quad \text{.....(11)},$$

where b and c are constants, their values being calculated from Fig. 5 and are given in the following table.

Table V

Kind of plates	Wave length of light	b	c	a
Ilford Spec. Rap. Panchr. Plate	500 μμ.	0.0000090	0.022	0.000031
Ilford Spec. Rap. Panchr. Plate	700	0.000019	0.019	0.000057
Eastman Universal Plate	450	−0.0000046	0.046	0.000038
Wratten & Wainwright Process Panchr. Plate	700	0.000016	0.0058	0.000034

Thus, as the result of these analyses of the characteristic curves the following empirical formula of density growth expressed as a function of the temperature is obtained:

$$D=D_m e^{at^2}\left\{1-e^{-(bt^2+c)E}\right\} \quad \text{.....(12)},$$

where D_m is the maximum density at 0°C., E is the exposure, t is the temperature of the dry plate in °C., and a, b and c are constants depending

on the wave length of the exposure light, time of development and properties of emulsion, where a decreases as the time of development increases, and b is negative for some rapid plates and positive for other plates.

The following table gives the values of the observed and calculated densities using equation (12) for Ilford Special Rapid Panchromatic Plate for light of $\lambda = 500\,\mu\mu$.

Table VI

Temp. / Exp.	15°C.		30°C.		40°C.		50°C.		60°C.		70°C.		80°C.	
	ob.	cal.	ob.	cal.	ob.	cal.	ob.	cal.	ob.	cal.	ob.	cal.	ob.	cal.
2^2	0.18	0.18	0.23	0.23	0.29	0.27	0.34	0.34	0.41	0.42	0.48	0.52	0.63	0.64
2^3	0.36	0.34	0.43	0.42	0.51	0.51	0.63	0.63	0.75	0.74	0.92	0.93	1.15	1.12
2^4	0.66	0.62	0.76	0.76	0.85	0.89	1.08	1.07	1.28	1.26	1.48	1.48	1.71	1.70
2^5	1.10	1.06	1.20	1.23	1.34	1.39	1.53	1.59	1.82	1.82				

The coincidence is pretty good, showing that this formula holds from 10°C. to 80°C..

In conclusion, the author wishes to express his thanks to Prof. M. Kimura for his kind advice and the great interest he has taken in the present investigation, and the author's thanks are also due to President T. Maruyama of the Konan College for his good offices.

Quantitative Analysis of Phosphoric Acid, Part I. Determination as Magnesium Pyrophosphate

By

Masayoshi Ishibashi

(Received October 30, 1928)

Since the method of determining phosphoric acid as magnesium pyrophosphate was proposed by B. Fresenius[1] a great number of investigations has been carried out by many authors with the object of finding the best condition under which a constant and exact result may be secured. It was soon found out that such is, however, no easy task. The thorough investigation critically carried out both by D. Balarew[2] and Z. Kalaoglanow[3] showed that of all the methods hitherto proposed, only B. Schmitz's method[4] of precipitating magnesium ammonium phosphate from an acidic solution with ammonia at high temperature gives a reliable result. At present Schmitz's method is generally regarded as the best analytical process for determining phosphoric acid and is described as such in many text-books. The method is still not without some defects: first it is not directly applicable for determination of phosphoric acid separated as ammonium phosphomolybdate; secondly, by this method the value of phosphoric acid is often found too high, unless strict attention be payed to the quantity of ammonium chloride which must always be in an excess but not more than a certain limit (see below); thirdly, as it is worked at high temperature some precipi-

1 Zs. anal. Chem., **6**, 403 (1869).

2 Zs. anorg. u. allg. Chem., **101**, 229 (1917); **102**, 241 (1917); **103**, 73 (1918); **104**, 53, (1918); **106**, 268 (1919); **117**, 91 (1921).

3 Zs. anal. Chem., **57**, 353, 497 (1918).

4 Ibid., **45**, 512 (1906); **65**, 46 (1924).

tates adhere to the wall of the vessel so firmly that they can by no means be rubbed off mechanically and should therefore be dissolved in hydrochloric acid and reprecipitated once again, thus making the process very tedious. Moreover, magnesium ammonium phosphate first separated out from an acidic solution by addition of ammonia has a tendency to become a colloidal precipitate. As it can not be transformed into the crystalline form by mere heating the precipitate must be redissolved in hydrochloric acid in order to renew the precipitation. Sometimes we have to repeat the process several times before the crystalline precipitate is obtained, and as the consequence of such repetition, more ammonium chloride accumulates in the solution than the allowable limit. The method of precipitating magnesium ammonium phosphate at ordinary temperature is accompanied by many sources of error, such as precipitating normal magnesium phosphate $Mg_3(PO_4)_2$ and magnesium tetra-ammonium diphosphate $Mg\{(NH_4)_2PO_4\}_2$ together with it.

The present writer thought that it would not be impossible to get rid of these sources of error by properly controlling the compositiou of the magnesia mixture on the one hand and by keeping the P_H at some appropriate value on the other, and after having carrid out many experiments to see their influence upon the analytical results ultimately succeeded in obtaining a simple but a very trustworthy procedure.

Experimental

I. Critical Study

In order to test the various methods proposed by many authors such as B. Schmitz[1], K. K. Järvinen[2], G. Jörgensen[3] and others, and to find out, if possible, the cause of errors in these methods, determination of phosphoric acid in ammonium phosphate was performed according to their directions, in each case 50 ml of a solution which contained 10.1167 grams of the phosphate in 1 litre being taken.

Schmitz's method

	$Mg_2P_2O_7$		P_2O_5	Error
	grm.	colour	%	%
Ordinary temperature	0.4262	white	53.75	—0.02
	0.4260	„	53.73	—0.04

1 Loc. cit.
2 Zs. anal. Chem., **44**, 333 (1905).
3 Ibid., **45**, 278 (1906); **50**, 336 (1611); **66**, 209 (1926).

High temperature	0.4629	,,	58.38	+4.61
	0.4607	,,	58.10	+4.35

Järvinen's method

The fine crystalline precipitates were left to stand for one, two or fifteen hours.

	Hours of standing	Ignited residue			$Mg_2P_2O_7$	P_2O_5	Error
		grm.	colour	grm. of $Mg(PO_3)_2$ (insoluble in HCl)	grm.	%	%
Ordinary temperature	1	0.4233	white	0.0053	0.4245	53.54	—0.23
	2	0.4241	,,	0.0044	0.4251	53.61	—0.16
	15	0.4259	,,	0	0.4259	53.71	—0.06
High temperature	1	0.4595	,,	0	0.4595	57.95	+4.18
	15	0.4586	,,	0	0.4586	57.84	+4.07

Jörgensen's method

Ordinary temperature	1	0.4235	,,	0.0062	0.4249	53.59	—0.18
	15	0.4260	,,	0	0.4260	53.73	—0.04
High temperature	1	0.4655	,,	0	0.4655	58.71	+4.94
	15	0.4630	,,	0	0.4630	58.39	+4.62

The only reliable ordinary temperature method is that of Schmitz, while those of other authors give satisfactory results only when the precipitates of magnesium ammonium phosphate are left to stand for a long time. At high temperatures all methods tend to yield a positive error, the cause of which may be attributed to the formation of normal magnesium phosphate. Kalaoglanow[1] assumes the formation of $(MgCl)_4P_2O_7$, $(MgCl)_3PO_4$ and $Mg_3(PO_4)_2$ as the cause of the positive error, but according to the writer's experiments though normal phosphoric acid was detected by Tollen's reaction, the presence of chlorine was in no case observed. The same author also assumes the decomposition of magnesium ammonium phosphate into the single phosphates at high temperatures and tries to explain why too high values of phosphoric acid are found in the high temperature method. To see if such really be the case the precipitate of magnesium ammonium phosphate was heated to about 75° in a water bath or to boiling temperature in a sand bath before filtration, but the formation of normal phosphate was never observed.

1 Loc. cit.

Heated in a water bath	$Mg_2P_2O_7$	P_2O_5	Diff.
min.	grm.	%	%
30	0.4260	53.73	−0.04
60	0.4260	53.73	−0.04
Heated in a sand bath			
15	0.4264	53.78	+0.01
20	0.4263	53.76	−0.01

As is seen in the following table, it was found that the formation of the normal phosphate at high temperatures could be prevented by adding an excess of ammonium chloride; it gives the best result when the molar ratio of ammonium chloride to magnesium chloride is maintained at about 30. If more ammonium chloride than that is present it tends to dissolve magnesium ammonium phosphate and thus becomes a cause of negative error.

Mol. Ratio	$Mg_2P_2O_7$		P_2O_5	Diff.
$NH_4Cl : MgCl_2$	grm.	Tollen's Reaction	%	%
22	0.4425	distinct	55.80	+2.03
26	0.4333	,,	54.67	+0.90
29	0.4263	trace	53.76	−0.01
37	0.4226	none	53.30	−0.47
44	0.4194	none	52.88	−0.89

The ordinary temperature methods of Järvinen and Jörgensen are both accompanied by a negative error, as was stated before, and the contamination of magnesium ammonium phosphate with magnesium tetra-ammonium diphosphate is generally considered to be the cause. The latter phosphate when ignited changes not to magnesium pyrophosphate but to the metaphosphate and thus lowers the value of phosphoric acid:

$$Mg\{(NH_4)_2PO_4\}_2 = Mg(PO_3)_2 + 4NH_3 + 2H_2O$$

The present writer thought that the formation of magnesium tetra-ammonium diphosphate is unavoidable unless magnesium is present in an excess far greater than to correspond to the ratio $Mg : PO_4$, and that it may gradually be transformed into magnesium ammonium phosphate when it is left to stand long with its mother liquor or heated. To confirm this view, pure magnesium ammonium phosphate was dissolved in dil. hydrochloric acid, and from this solution, to which some ammonium chloride had been added, magnesium ammonium phosphate was again precipitated with ammonia. The magnesium pyrophosphate from magnesium ammonium phosphate thus obtained was always observed to contain magnesium metaphosphate, the quantity of which, however,

became the less the longer the magnesium ammonium phosphate was left to stand with the mother liquor, as shown in the following table.

Hours of standing	Ignited residue grm.	colour	$Mg(PO_3)_2$	$Mg_2P_2O_7$ grm.	H_3PO_4 in the filtrate	P_2O_5 %	Diff. %
1	0.4186	white	0.0080	0.4204	+	53.02	−0.75
2	0.4227	,,	0.0067	0.4242	+	53.50	−0.27
5	0.4250	,,	0.0015	0.4253	+	53.64	−0.13
15	0.4262	,,	0	0.4262	0	53.75	−0.02
When heated in a water bath for an hour and left to stand:							
5	0.4259	,,	0	0.4259	0	53.71	−0.06
5	0.4261	,,	0	0.4261	0	53.74	−0.03

From this it was made clear how the precipitation reaction of magnesium ammonium phosphate should be conducted, how the precipitates should be treated before filtration, and also why Schmitz's method gave more accurate results than Jörvinen's and Jörgensen's.

The present writer was also able to confirm D. Balarew's opinion[1] that magnesium metaphosphate is formed by the interaction of magnesium pyrophosphate and phosphoric acid or ammonium phosphate, and also H. Neubauer's view[2] that magnesium metaphosphate gradually changes into the pyrophosphate when strongly ignited for a long time; 0.0405 grm. of magnesium metaphosphate lost 0.0159 grm. and became constant when ignited for 5 hours and a half (calculated loss = 0.0158 grm.).

II. Study of Magnesia Mixture

The magnesia mixture first used by B. Fresenius[3] for determination of phosphoric acid was an ammoniacal solution containing magnesium sulphate and ammonium chloride in molecular proportion. This, however, never gave exact results though a great many trials were made by several authors[4]. In 1873 O. Abesser, W. Jani and M. Märcker[5] succeeded in greatly improving the method by using a magnesia mixture in which magnesium chloride was substituted for magnesium sulphate

1 Loc. cit.
2 Zs. anal. Chem., **2**, 45 (1892).
3 Loc. cit.
4 Kubel: Zs. anal. Chem., **8**, 125 (1869).
Kissel: Ibid., **8**, 165 (1869); Heintz: Ibid., **9**, 16 (1870);
Schumann: Ibid., **11**, 382 (1872).
5 Ibid., **12**, 239 (1873).

with the following compositions: 110 grm. $MgCl_26H_2O$ + 140 grm. NH_4Cl + 700 grm. conc. ammonia water + 1300 grm. water. The proportion of NH_4Cl to $MgCl_2$ adopted by different authors for preparation of the magnesia mixture is quite different; for example F. A. Gooch and Martha Austin[1] used 50 grm. of NH_4Cl to 110 grm. of $MgCl_26H_2O$, while Järvinen[2] took 53 grm. of NH_4Cl and 102 grm. of $MgCl_26H_2O$. The latter author first paid attention to the acidity of the phosphate solution used for analysis and also that of the magnesia mixture. He made the phosphate solution faintly alkaline and the magnesia mixture just neutral with ammonia, and after adding the former solution to the latter shaking it the while, finally added sufficient ammonia to make the precipitation of magnesium ammonium phosphate complete.

In all the investigations of these authors, the study of how the precipitation of magnesium ammonium phosphate is related to the composition and also to the acidity of the magnesia mixture seems still insufficient. The present writer therefore undertook an investigation of these two points using Kahlbaum's ammonium phosphate "Zur Analyse mit Garantieschein."

10.1167 grm. of the phosphate were dissolved in 1 litre and 50 ml of the solution were taken for each determination. A molar solution of magnesium chloride and about 5 molar solution of ammonium chloride with the acidity $P_H = 5$ were taken, and these were added in different proportions to 50 ml of the above phosphate solution, when a minute crystalline precipitate of magnesium ammonium phosphate separated out. Then dilute ammonia water of 2.5 % concentration was slowly added, the mixture being well shaken all the while, till the phenolphthalein added beforehand became faintly coloured. About 10 ml of 20 % ammonia were now poured in, and after having been left to stand for an hour the solution was filtered, and the precipitate was washed with 2.5 % ammonia, dried and then ignited as usual. The results were as summarized in Table I.

It may be concluded from the table that the molecular ratio of ammonium chloride to magnesium chloride in the magnesia mixture should best be maintained between 5 and 15 (No. 1—No. 9), while that of magnesium chloride to phosphoric acid may be in the range between 1.3 and 10.5 (No. 10—No. 15). As to the reason why such an excess of ammonium chloride is needed, specially when worked at high temperature,

1 Zs. anorg. Chem., **20**, 133 (1899).
2 Zs. anal. Chem., **43**, 279 (1904).

Tbale I

No.	Water added	Magnesia Mixture						$Mg_2P_2O_7$		P_2O_5	Diff.
		$MgCl_2$			NH_4Cl						
	ml	ml	grm.	mol. ratio to $(NH_4)_2HPO_4$	ml	grm.	mol. ratio to $MgCl_2$	grm.	colour	%	%
1	10	7	0.67	1.8	7	1.88	5	0.4262	white	53.75	−0.02
2	10	„	„	„	10	2.68	7	0.4261	„	53.74	−0.03
3	10	„	„	„	14	3.75	10	0.4261	„	53.74	−0.03
4	10	„	„	„	14	3.75	10	0.4259	„	53.71	−0.06
5	5	„	„	„	21	5.65	15	0.4259	„	53.71	−0.06
6	5	„	„	„	21	5.65	15	0.4260	„	53.73	−0.04
7	5	„	„	„	28	7.50	20	0.4259	„	53.71	−0.06
8	—	„	„	„	35	9.38	25	0.4253	„	53.63	−0.14
9	—	„	„	„	35	9.38	25	0.4255	„	53.66	−0.11
10	—	5	0.48	1.3	7	1.88	7	0.4263	„	53.76	−0.01
11	—	10	0.95	2.6	14	3.75	7	0.4264	„	53.78	+0.01
12	—	15	1.43	3.9	21	5.65	7	0.4262	„	53.75	−0.02
13	—	20	1.90	5.2	28	7.50	7	0.4263	„	53.76	−0.01
14	—	30	2.86	7.8	42	11.28	7	0.4260	„	53.73	−0.04
15	—	40	3.81	10.5	56	15.04	7	0.4262	„	53.75	−0.02
16	50	7	0.67	1.8	10	2.68	7	0.4261	„	53.74	−0.03
17	100	7	0.67	1.8	10	2.68	7	0.4260	„	53.73	−0.04
18	200	7	0.67	1.8	10	2.68	7	0.4261	„	53.74	−0.03
19	300	7	0.67	1.8	10	2.68	7	0.4261	„	53.74	−0.03
20	400	7	0.67	1.8	10	2.68	7	0.4267	„	53.81	+0.04
21	500	7	0.67	1.8	10	2.68	7	0.4271	„	53.86	+0.09
22	600	7	0.67	1.8	10	2.68	7	0.4282	„	54.00	+0.23

and at the same time its amount must be kept under a certain limit has already been discussed in the part devoted to critical study. The experiments from No. 16 to No. 22 were conducted to find out the influence of dilution, which was found to give a marked positive error due to the formation of normal magnesium phosphate when the solution becomes too much diluted.

From the results thus studied it was found that the magnesia mixture which give the most exact result in the determination of phosphoric acid should be prepared in the following way: 50 grm. of crystalline magnesium chloride and 100 grm. of ammonium chloride (the molar ratio of the latter to the former is 7.6) are dissolved together in water, and to this solution conc. ammonia water is added till phenolphthalein added beforehand becomes distinctly red. After standing 2 or 3 days the solution is filtered, if necessary, and then dil. hydrochloric acid is added to it just to decolourize the phenolphthalein. The solution is now diluted with water to one litre and its acidity is so adjusted that the P_H value lies between 5 and 6. This is done without any difficulty by aid of methyl red ($P_H = 4.4 - 6.3$) or p-nitrophenol ($P_H = 5.0 - 7.9$).

III. On the Suitable Acidity of the Phosphate Solution

For the precipitation of magnesium ammonium phosphate, the phosphate solution made alkaline with ammonia was generally used. But it was soon found that the precipitates often become contaminated with magnesium tetra-ammonium diphosphate which changes into magnesium metaphosphate on ignition and becomes a cause of negative error.

B. Schmitz's modified method[1], in which phosphate solution previously acidified with hydrochloric acid is used, is not directly applicable for determination of phosphoric acid separated as ammonium phosphomolybdate. Moreover, when the acid is very concentrated, much ammonium chloride is produced on addition of ammonia and this tends to dissolve magnesium ammonium phosphate. The present writer, therefore, thought it necessary first to determine the P_H value of the phosphate solution from which the quantitative precipitation of magnesium ammonium phosphate is possible. 50 ml of the ammonium phosphate solution described in section I were taken for each experiment and the relation of the acidity to the accuracy of analysis was studied. The results are shown in Table II.

From the table it is clearly seen that the P_H value of the phosphate solution should be kept greater than 4.4 and less than 8.3, otherwise the value of phosphoric acid is found lower. For the sake of security the present writer always maintained it between 6.0 and 8.3, because the solution of such acidity may safely be used in the presence of molybdic acid too. The above safe range of acidity can conveniently be

1 Loc. cit.

obtained by using methyl red ($P_H = 4.4-6.3$), p-nitrophenol ($P_H = 5.0-7.9$) bromthymolblue ($P_H = 6.0-7.6$) or neutral red ($P_H = 6.9-8.0$).

Table II

No.	P_H	Mag. mixture	$Mg_2P_2O_7$	P_2O_5	Diff.
		ml	grm.	%	%
1	1.3	25	0.4260	53.73	−0.04
2	1.3	„	0.4259	53.71	−0.06
3	4.4	„	0.4261	53.74	−0.03
4	4.4	„	0.4264	53.78	+0.01
5	4.4	„	0.4262	53.75	−0.02
6	6.0	„	0.4262	53.75	−0.02
7	6.0	„	0.4261	53.74	−0.03
8	6.0	„	0.4263	53.76	−0.01
9	7.5	„	0.4262	53.75	−0.02
10	7.5	„	0.4261	53.74	−0.03
11	7.5	„	0.4264	53.78	+0.01
12	8.3	„	0.4263	53.76	−0.01
13	8.3	„	0.4261	53.74	−0.03
14	8.3	„	0.4262	53.75	−0.02
15	9.3	„	0.4255	53.66	−0.11
16	9.3	„	0.4254	53.65	−0.12
17	11.0	„	0.4245	53.54	−0.23
18	11.0	„	0.4249	53.59	−0.18

IV. Influence of Temperature on the Precipitation of Magnesium Ammonium Phosphate

As was stated in the previous section the composition and acidity of the magnesia mixture and also the acidity of the phosphate solution which are most suitable for quantitative determination of phosphoric acid were determined. By using solutions having such composition and acidity, quantitative analyses were carried out at different temperatures in order to ascertain which temperature is most preferable. It is generally known, as was stated in section I, that at higher temperatures a somewhat higher

value is often obtained for phosphoric acid and the form of magnesium ammonium phosphate is very liable to become colloidal. Such a result was also found in these experiments, as may be observed in Table III (No. 1—No. 2).

Table III

For each determination, 50 ml of a solution containing 10.1167 grm. of $(NH_4)_2HPO_4$ in 1 litre were taken.

No.	Temp.	Mag. mixture	$Mg_2P_2O_7$		P_2O_5	Diff.
		ml	grm.	colour	%	%
1	70°—75°	25	0.4520	slightly gray	57.00	+3.23
2	70°—75°	25	0.4470	slightly gray	56.37	+2.60
3	18°→90°	25	0.4266	slightly gray	53.80	+0.03
4	18°→90°	25	0.4260	slightly gray	53.73	−0.04
5	22°—25°	25	0.4264	white	53.78	+0.01
6	22°—25°	25	0.4262	white	53.75	−0.02
7	13°—15°	25	0.4261	white	53.74	−0.03
8	13°—15°	25	0.4263	white	53.76	−0.01

At temperatures down to 35° the precipitates of magnesium ammonium phosphate were seen to be partly colloidal and became crystalline only after standing a long time. When worked at temperatures lower than 35° the precipitates were always obtained in crystalline form, and exact results were obtained (No. 5—No. 8). It is very interesting to note that analysis of phosphoric acid may also be conducted at high temperatures without any hindrance in the following way: The phosphate solution is first mixed with the magnesia mixture at ordinary temperatures, say 18°, and the solution in which some crystalline precipitates are formed is then heated to a high temperature, say 90°, and then treated with ammonia (No. 3—No. 4).

V. Time of Precipitation and of Standing

The time required for precipitation of magnesium ammonium phosphate and also the time allowed for the precipitates to stand influence the results of analysis in no small degree. A series of experiments was carried out in the following way: 50 ml of the solution containing 10.1167 grm. of ammonium phosphate in 1 litre were mixed with 25 ml

of the magnesia mixture as usual, when a small quantity of a fine crystalline precipitate of magnesium ammonium phosphate separated out. Now 2.5 % ammonia water was added to it at different intervals varying from one to five minutes, till the phenolphthalein added beforehand became distinctly red, and the solution was left to stand for certain times after addition of 10 ml of 20 % ammonia. It is seen from Table IV that as the time required for precipitation, that is, the time of adding the 2.5 % ammonia water, 3–5 minutes is sufficient and 30 minutes for the time the precipitates are left to stand.

Table IV

No.	Mag. mixture	Time required for precipitation	Time of standing	$Mg_2P_2O_7$	P_2O_5	Diff.
	ml	min.	min.	grm.	%	%
1	25	3–5	5	0.4256	53.67	−0.10
2	25	3–5	10	0.4260	53.73	−0.04
3	25	3–5	20	0.4262	53.75	−0.02
4	25	3–5	30	0.4263	53.76	−0.01
5	25	3–5	60	0.4263	53.76	−0.01
6	25	1–2	60	0.4259	53.71	−0.06

VI. Procedure for Precipitating Magnesium Ammonium Phosphate and Composition of the Precipitates

From what has been described so far we can deduce the following procedure for determining phosphoric acid as the best of all methods hitherto known.

The acidity of the phosphate solution whose concentration may be $\frac{1}{10}-\frac{1}{100}$ molar is so regulated that one or two drops of p-nitrophenol added to it show a slightly yellow colour, and to this solution the magnesia mixture prepared according to the manner described in section II is added in an excess and well agitated, whereupon a fine crystalline precipitate begins to separate out. Now 2.5 % ammonia water is added, the mixture being well shaken all the while, at such a rate as to complete the precipitation in 3—5 minutes, till the phenolphthalein added beforehand becomes distinctly red. About one-seventh volume of 20 % ammonia is now added and the solution left to stand for about 30 minutes. After

filtration, the precipitates are washed with 2.5 % ammonia water till they become free from chloride, and dried, ignited and finally weighed as usual.

To know whether the precipitate is really of the composition $MgNH_4PO_4 \cdot 6H_2O$, it was analysed, with the following results:

The ppte taken	$\frac{N}{10}$—HCl required to neutralize ammonia evolved	NH_3 (%) found	calc.
0.4828 grm.	19.50 ml	6.88	6.94
0.5100 „	20.72 „	6.92	

The quantity of water of crystallization was calculated from that of magnesium pyrophosphate produced from a known quantity of the sample:

The ppte taken	$Mg_2P_2O_7$	$MgNH_4PO_4 = a$	$xH_2O = b$	$x\left(=\frac{b \times 137.46}{a \times 18.016}\right)$
0.6370 grm.	0.2886 grm.	0.3563 grm.	0.2807 grm.	6.0110
0.6370 „	0.2888 „	0.3565 „	0.2805 „	6.0036
1.3730 „	0.6228 „	0.7688 „	0.6042 „	5.9966

VII. Influence of Other Salts present

As to the influence of various substances on the precipitation of magnesium ammonium phosphate much is not yet known except that potassium ion and sulphation become the cause of positive error, while acetation and too large an excess of ammonium chloride cause negative error. The present writer quantitatively studied the influence of sodium chloride, potassium chloride, sodium nitrate, sodium sulphate, ammonium sulphate, sodium acetate, formic acid, oxalic acid, citric acid, tartaric acid, ammonium molybdate and ammonium chloride upon the reaction, using 50 ml of the ammonium phosphate solution and 25 ml of the magnesia mixture for each determination. The results of the experiments are given in Table V.

NaCl——Sodium chloride seems to retard the precipitation of magnesium ammonium phosphate, but this has no bad effect if the precipitate is left to stand for a long time with the mother liquor (No. 1—No. 6).

KCl——This affects the result of analysis in no small degree, giving a higher value for phosphoric acid (No. 7—No. 13). From the fact that the precipitate of magnesium ammonium phosphate contains potassium but not chlorine it appears very probable that some magnesium potassium phosphate is formed together with the corresponding ammonium salt so as to form a mixed crystal. When once crystallized in the form of

Table V

No.	Salt mixed		Time of standing	$Mg_2P_2O_7$		P_2O_5	Diff.
	Name	grm.	min.	grm.	colour	%	%
1	NaCl	3.0	30	0.4258	white	53.70	−0.07
2	„	3.0	120	0.4264	„	53.78	+0.01
3	„	6.0	30	0.4249	„	53.59	−0.18
4	„	6.0	150	0.4263	„	53.76	−0.01
5	„	9.0	50	0.4256	„	53.67	−0.10
6	„	9.0	150	0.4262	„	53.75	−0.02
7	KCl	6.0	120	0.4372	„	55.14	+1.37
8	„	4.0	120	0.4344	„	54.78	+1.01
9	„	2.0	120	0.4306	„	54.30	+0.53
10	„	1.0	60	0.4282	„	54.00	+0.23
11	„	0.6	60	0.4273	„	53.89	+0.12
12	„	0.2	60	0.4264	„	53.78	+0.01
13	„	0.1	60	0.4261	„	53.74	−0.03
14	$NaNO_3$	6.0	30	0.4262	„	53.75	−0.02
15	„	6.0	120	0.4262	„	53.75	−0.02
16	„	9.0	120	0.4263	„	53.76	−0.01
17	Na_2SO_4	6.0	600	0.4316	„	54.43	+0.66
18	„	6.0	120	0.4318	„	54.46	+0.69
19	„	4.0	120	0.4317	„	54.44	+0.67
20	„	2.0	60	0.4308	„	54.33	+0.56
21	„	1.0	60	0.4279	„	53.97	+0.20
22	„	0.6	60	0.4273	„	53.89	+0.12
23	„	0.2	60	0.4264	„	53.78	+0.01
24	$(NH_4)_2SO_4$	6.0	120	0.4348	„	54.83	+1.06
25	$C_2H_3O_2Na$	6.0	120	0.4218	„	53.20	−0.57
26	„	2.0	120	0.4235	„	53.41	−0.36
27	„	0.6	120	0.4248	„	53.57	−0.20
28	„	0.2	120	0.4250	„	53.60	−0.17
29	„	0.1	120	0.4255	„	53.66	−0.11
30	„	0.06	120	0.4258	„	53.70	−0.07
31	„	0.02	120	0.4262	„	53.75	−0.02
32	H_2CO_2	6.10	120	0.4263	„	53.76	−0.01
33	„	3.66	120	0.4262	„	53.75	−0.02
34	$H_2C_2O_4$	1.5	60	0.4261	„	53.74	−0.03
35	$H_8C_6O_7$	2.5	120	0.4283	grayish black	54.02	+0.25
	after ignition again with HCl			0.4265	white	53.79	+0.02
36	„	0.5	120	0.4272	grayish black	53.88	+0.11
	after ignition again with HCl			0.4266	white	53.80	+0.03

No.	Salt mixed		Time of standing	$Mg_2P_2O_7$		P_2O_5	Diff.
	Name	grm.	min.	grm.	colour	%	%
37	„	0.15	120	0.4274	grayish black	53.90	+0.13
	after ignition again with HCl			0.4265	white	53.79	+0.02
38	„	0.08	120	0.4273	grayish black	53.89	+0.12
	after ignition again with HCl			0.4266	white	53.80	+0.03
39	„	0.05	120	0.4274	grayish black	53.90	+0.13
	after ignition again with HCl			0.4265	white	53.79	+0.02
40	$H_6C_4O_6$	2.5	120	0.4338	grayish black	54.71	+0.94
	after ignition again with HCl			0.4310	grayish black	54.36	+0.59
	after ignition twice with HCl			0.4265	white	53.79	+0.02
41	„	0.15	120	0.4275	grayish black	53.92	+0.15
	after ignition again with HCl			0.4265	white	53.79	+0.02
42	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	2.40	30	0.4254	white	53.65	−0.12
43	„	2.40	120	0.4262	„	53.75	−0.02
44	„	4.80	120	0.4265	„	53.79	+0.02
45	NH_4Cl	5.36	120	0.4259	„	53.71	−0.06
46	„	10.72	120	0.4235	„	53.41	−0.36

$MgNH_4PO_4\cdot 6H_2O$ it undergoes no change even when left to stand long in a solution containing KCl.

KCl	$Mg_2P_2O_7$	P_2O_5	Diff.
4.0 grm.	0.4262 grm.	0.2719 grm.	−0.02 %
6.0 „	0.4260 „	0.2718 „	−0.04 „

$NaNO_3$——No influence (No. 14—No. 16).

Na_2SO_4 and $(NH_4)_2SO_4$——Both give rise to positive error, and the precipitate of magnesium ammoniun phosphate was always found to contain sulphuric acid, as, for example, from magnesium pyrophosphate obtained in the experiment shown in No. 24 0.0118 grm. of $BaSO_4$ was produced. No bad influence was observed if these sulphates were added after the precipitation of magnesium ammonium phosphate had been completed.

Na_2SO_4	$Mg_2P_2O_7$	P_2O_5	Diff.
6.0 grm.	0.4363 grm.	0.2720 grm.	−0.01 %

The reason why Fresenius'[1] and Winkler's[2] methods of using magnesium sulphate in the preparation of the magnesia mixture do not give satisfactory results will now be clear.

$NaO_2C_2H_3$——Though sodium acetate does not dissolve magnesium

1 Loc cit.

2 J. Soc. chem. Ind., 391 A. (1919).

ammonium phosphate, it makes the precipitation of the latter incomplete (No. 25—No. 31). This incompleteness could never be improved by allowing the precipitate to stand even for 20 hours.

$(NH_4)_2HPO_4$	$Mg_2P_2O_7$	P_2O_5	Diff.
0.5058 grm.	0.4217 grm.	53.18 %	−0.59 %

H_2CO_2 and $H_2C_2O_4$——Both were found to have no effect (No. 32—No. 34).

$H_3C_6O_7$——When citric acid exists in the solution it is adsorbed in the precipitate of magnesium ammonium phosphate and consequently magnesium pyrophosphate is found higher in its value and coloured grayish black (No. 35—No. 39). This hindrance may, however, be easily removed either by igniting the pyrophosphate with a few drops of conc. hydrochloric acid or nitric acid or by dissolving the precipitate of magnesium ammonium phosphate in dil. hydrochloric acid and again precipitating.

	$(NH_4)_2HPO_4$	$Mg_2P_2O_7$	P_2O_5	Diff.
1 st precipitation	0.5058 grm.	0.4266 grm.	53.80 %	+0.03 %
2 nd „	„	0.4263 „	53.76 %	−0.01 %

$H_6C_4O_6$——The effect of tartaric acid on the analysis of phosphoric acid was observed to be analogous with that of citric acid (No. 40—No. 41).

$(NH_4)_6Mo_7O_{24}4H_2O$——Though its action is to retard the precipitation of magnesium ammonium phosphate, the complete precipitation may be brought about by simply keeping the precipitate with the mother liquor for 2 hours (No. 42—No. 44).

NH_4Cl——This becomes a cause of negative error only when it exists in too large an excess as was stated before (No. 45—No. 46).

Summary

1. With the object of finding a trustworthy procedure for analysis of phosphoric acid a critical study of various methods for precipitating magnesium ammonium phosphate hitherto proposed was carried out and the sources of error were experimentally sought.

2. The relation of the composition and acidity of the magnesia mixture to the accuracy of the analytical result was examined, and the magnesia mixture giving the most satisfactory result was prepared.

3. The dilution and acidity of the phosphate solution to be taken for analysis were determined.

4. Influence of various substances such as NaCl, KCl, $NaNO_3$, Na_2SO_4, $(NH_4)_2SO_4$, $NaO_2C_2H_3$, H_2CO_2, $H_2C_2O_4$, $H_8C_6O_7$, $H_6C_4O_6$, $(NH_4)MoO_4$ and NH_4Cl on the precipitation of magnesium ammonium phosphate were investigated.

5. As the result of this investigation a simple and exact procedure for precipitating phosphoric acid as magnesium ammonium phosphate was found out.

The writer wishes here to express his sincere thanks to Professor M. Matsui, at whose suggestion the work was carried out.

Quantitative Analysis of Phosphoric Acid, Part II. New Gravimetric and Volumetric Methods

By

Masayoshi Ishibashi

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The method of determining manganese as its pyrophosphate was studied by W. Gibbs[1] and by F. A. Gooch and Martha Austin[2], and it is now practically used for analysis. The reaction of precipitating phosphoric acid as manganous ammonium phosphate, however, has long been regarded as unapplicable for the determination of phosphoric acid, because manganese undergoes spontaneous oxidation in an alkaline solution and is partly precipitated as brown manganous acid. According to the present writer's experiment the formation of manganous acid can never be prevented by the addition of an excess of ammonium chloride. In one experiment the molar ratio of ammonium chloride to manganous chloride was made as high as 400, and still it was not effective; the manganous acid was observed to begin its precipitation after about two hours.

After having made several trials the present writer finally succeeded in finding out that the formation of manganous acid could entirely be prevented by the addition of a small quantity of hydroxylamine, and as a consequence the precipitation of phosphoric acid as manganous ammonium phosphate could be utilised as a new gravimetric method for its determination. It was also found that the manganese in manganous ammonium phosphate can be exactly titrated with potassium permanganate, and this process may be employed as an excellent volumetric method for analysis of phosphoric acid.

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1 ZS. anal. Chem., **7**, 101 (1868).

2 ZS. anorg. Chem., **18**, 339 (1893); ZS. anal. Chem., **38**, 784 (1900).

Experimental

I. Gravimetric Method

In the experiments described below the following solutions were employed :

(a) Diammonium phosphate solution containing 10.0000 grams of Kahlbaum's ammonium phosphate " Zur Analyse mit Garantieshein " in one litre.

(b) A molar manganous chloride solution prepared by dissolving 198 grams of the crystalline salt in one litre.

(c) Ammonium chloride solution prepared by dissolving 268 grams of the chloride in water was made alkaline by the addition of a small quantity of conc. ammonia and diluted to one litre. After standing for 2 or 3 days it was filtered and acidified with hydrochloric acid till its reaction to methyl red was acid. This solution is nearly 5 molar and its P_H is about 5.

(d) 10 % hydroxylamine hydrochloride solution.

(e) The solution used for washing the precipitate was prepared as follows : to 500 ml of 1 molar ammonium chloride solution, 1 ml of the hydroxylamine solution above stated was added and the mixture was made alkaline with ammonia till phenolphthalein added to it beforehand, became distinctly red.

(f) Ammonia waters of 20 % and 1 %.

Procedure for precipitating manganous ammonium phosphate :—

To the phosphate solution, manganous chloride and ammonium chloride are added in an excess together with a small quantity of hydroxylamine hydrochloride and well stirred. The acidity of the solution should be such that the precipitate of manganous ammonium phosphate is produced only in a small quantity. If, therefore, the precipitate is produced in a large quantity, it must be redissolved in hydrochloric acid. Now the solution in which either none or a small quantity of the precipitate is suspended is heated nearly to boiling point, and dilute ammonia water is added drop by drop, the solution being well agitated all the while, when a crystalline precipitate with silky lustre is produced. Some conc. ammonia water is now added to make the solution strongly alkaline and the whole is left to cool for about 2 hours and filtered. The precipitate is washed with the washing solution above stated and then with 1 % ammonia water, and finally dried, ignited and weighed as usual. It must be remembered that if the reaction of precipitating manganous ammonium phosphate is conducted at ordinary temperature the precipitate takes a

colloidal form and contains no small quantity of $Mn_3(PO_4)_2$. If this normal phosphate is once formed in a solution containing manganous chloride in an excess it can never be transformed into manganous ammonium phosphate by mere heating. If, however, the manganese present is just equivalent to the phosphoric acid or less, the transformation can be brought about completely by heating, and this may be counted as another reason why phosphoric acid could not hitherto be determined as manganous pyrophosphate.

1. *Relative Amounts of Manganous Chloride and Ammonium Chloride*

To find out the most suitable amounts of manganous chloride and ammonium chloride which should be taken for precipitation of manganous ammonium phosphate and also to learn the influence of dilution of the sample solution, a series of experiments were carried out the results of which are shown in Table I.

Table I

For each determination 25 ml of the ammonium phosphate solution and 0.3 ml of the hydroxylamine hydrochloride solution were taken.

No.	Water added ml	$MnCl_2$			NH_4Cl			$Mn_2P_2O_7$	P_2O_5 (53.77%)	
		ml	grm.	Mol. ratio to $(NH_4)_2HPO_4$	ml	grm.	Mol. ratio to $MnCl_2$	grm.	%	Diff.
1	75	5	0.629	2.6	25	6.9	25	0.2750	55.04	+1.27
2	50	"	"	"	50	13.4	50	0.2699	54.02	+0.25
3	25	"	"	"	75	19.6	75	0.2686	53.76	−0.01
4	10	"	"	"	90	24.1	90	0.2686	53.76	−0.01
5	—	"	"	"	100	26.8	100	0.2687	53.78	+0.01
6	—	"	"	"	125	33.5	125	0.2688	53.80	+0.03
7	—	"	"	"	150	40.2	150	0.2688	53.80	+0.03
8	—	"	"	"	200	53.6	200	0.2682	53.69	−0.08
9	—	3	0.378	1.6	60	16.1	100	0.2686	53.76	−0.01
10	—	5	0.629	2.6	100	26.8	100	0.2687	53.78	+0.01
11	—	10	1.259	5.3	200	53.6	100	0.2687	53.78	+0.01
12	—	20	2.518	10.6	400	107.2	100	0.2687	53.78	+0.01
13	100	5	0.629	2.6	100	26.8	100	0.2688	53.80	+0.03
14	200	5	0.629	2.6	100	26.8	100	0.2692	53.88	+0.11
15	300	5	0.629	2.6	100	26.8	100	0.2710	54.24	+0.47

From the above results we can draw the following conclusions:

1. Complete precipitation of phosphoric acid takes place when the molar ratio of ammonium chloride to manganous chloride lies between 75 and 125. Deficiency of ammonium chloride becomes a cause of positive error, phosphoric acid being partly precipitated in the form of normal manganous phosphate, while too great excess of this reagent produces negative error, as it tends to dissolve manganous ammonium phosphate (No. 1—No. 8).
2. The amount of manganous chloride does not much effect the exactness of analysis if it be present in an excess as is seen in No. 9—No. 12.
3. Analysis with too dilute solution is to be avoided, because from such solutions the value of phosphoric acid is often found too high owing to the precipitation of normal manganous phosphate (No. 13—No. 15).

2. *Influence of Various Salts on the Analysis*

The influence of various salts such as sodium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium citrate, ammonium tartrate and ammonium oxalate was examined. In each experiment, 25 ml of the phosphate solution were mixed with a definite quantity of the salt and this solution was treated with 5 ml of manganous chloride, 100 ml of ammonium chloride and 0.3 ml of hydroxylamine solution in the manner described before. The results are shown in Table II.

Table II

No.	Salt mixed		Time of standing	$Mn_2P_2O_7$		P_2O_5	Diff.	
	Name	grm.	hours	grm.	colour	%	%	
1	NaCl	3.0	2	0.2687	pale rose	53.78	+0.01	
2	KCl	2.0	2	0.2688	„	53.80	+0.03	
3	Na_2SO_4	2.0	2	0.2688	„	53.80	+0.03	
4	$NaNO_3$	3.0	2	0.2688	„	53.80	+0.03	
5	$C_2H_3O_2Na$	2.0	20	0.2686	„	53.76	−0.01	
6	Am. citrate	5.0	2	0.2511	„	50.26	−3.51	
7	„	2.5	2	0.2630	„	52.70	−1.07	
8	Am. tartrate	5.0	2	0.2806	grayish brown	56.16	+2.39	Phosphate was detected in the filtrate
9	„	2.5	3	0.2681	pale rose	53.66	−0.11	„
10	„	5.0	3	0.2676	„	53.56	−0.21	„
11	Am. oxalate	1.0	2	0.2717	„	54.32	+0.55	Phosphate was detected in the filtrate and in $Mn_2P_2O_7$
12	„	1.0	20	0.2797	„	55.98	+2.21	No phosphate in the filtrate
13	„		3	0.2687	„	53.78	+0.01	

NaCl, KCl, Na_2SO_4, $NaNO_3$.——These salts have no influence as is seen in No. 1—No. 4.

$C_2H_3O_2Na$.——This seems to retard the precipitation of manganous ammonium phosphate, so that the precipitate should be left to stand for a long time before filtration (No. 5).

Ammonium citrate.——This seems mainly to dissolve manganous ammonium phosphate (No. 6—No. 7).

Ammonium tartrate.——The action of this salt is twofold: tartrate is occluded (perhaps as manganous tartrate) in the precipitate of manganous ammonium phosphate so as to make the value of phosphoric acid very high (No. 8) and at the same time it has the effect of making the precipitation incomplete (No. 9 and No. 10). When therefore ammonium tartrate is added after the precipitation of manganous ammonium phosphate is completed, the value of phosphoric acid is found remarkably low.

Ammonium oxalate.——It retards the precipitation of manganous ammonium phosphate and forms some other phosphate which does not change into pyrophosphate. The former hindrance may be got rid of by long standing, but at the same time the latter hindrance becomes greater (No. 11—No. 12). The two hindrances may only be cleared away by means of double precipitation (No. 13).

3. *Influence of Ammonium Molybdate*

To examine the influence of ammonium molybdate on this method of phosphoric acid determination and to find out a convenient process by which its bad effect, if any, may be well prevented was a very interesting work for the present writer.

In an analysis conducted preliminarily with a phosphate solution containing 1.20 grams of ammonium molybdate, the precipitate was found to contain a considerable quantity of $MnMoO_4$. Though manganous molybdate dissolves in concentrated ammonia its complete separation from manganous ammonium phosphate could not be effected by merely washing with ammonia.

So the precipitation of the phosphate from a solution previously made strongly ammoniacal was tried in the hope that manganous molybdate would not separate out together with it from such a solution. To 25 ml of the phosphate solution made strongly ammoniacal 100 ml of the ammonium chloride solution, 2.4 grams of ammonium molybdate and 0.3 ml of hydroxylamine solution were added, and after heating the solutin

nearly to boiling point about 1 ml of the manganous chloride solution was added to it and well agitated, whereupon the precipitate formed became crystalline. Now a second 1 ml of manganous chloride solution was then added and agitated, and this process was repeated several times till the total quantity of manganous chloride attained the required excess. Sometimes manganous ammonium phosphate begins to become yellowish coloured. As this shows the formation of manganous molybdate, concentrated ammonia water must, in such a case, be again poured in to prevent its precipitation. Now the precipitate of manganous ammonium phosphate was filtered after about 2 hours' standing and treated as usual. Though all this was done with the utmost care, the precipitate was always faintly yellowish and the value of phosphoric acid was found 0.23–0.35 % higher.

It was therefore thought necessary to make double precipitation and for this purpose manganous ammonium phosphate was dissolved in dilute hydrochloric acid, and to this solution 2 ml of manganous chloride, 100 ml of ammonium chloride and 0.3 ml of hydroxylamine solution were again added and from this solution manganous ammonium phosphate was precipitated for the second time. The result was now quite satisfactory.

II. Volumetric Method

Titration of manganese with potassium permanganate according to the reaction

$$3Mn^{\cdot\cdot} + 2MnO_4 + 2H_2O = 5MnO_2 + 4H^{\cdot}$$

is now practically used for analysis as Guyard-Volhard's or Volhard-Wolff's method. In order to precipitate manganese completely as MnO_2, zinc sulphate or zinc oxide has generally been added to manganese solution. Recently B. Reinitzer and P. Conrath[1] stated that sodium acetate may replace the zinc salt or oxide with far better results, precipitating MnO_2 quicker and more completely.

Now it occurred to the present writer that if the above method could be applied for determining manganese in manganous ammonium phosphate it might conveniently be utilised as an indirect method for analysis of phosphoric acid. The result of experiments carried out with the purpose of confirming this view showed that phosphoric acid can thus be determined rapidly with an average error of ±0.1 % even when the acid is present in the small quantity of a few milligrams, as is described below.

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1 ZS. anal. Chem., **68**, 130 (1926

Procedure

Manganous ammonium phosphate produced from a known quantity of ammonium phosphate is dissolved in water acidified with 2 or 3 drops of sulphuric acid and after adding a suitable quantity of sodium acetate (about 2 grams for each 10 ml of $\frac{N}{10}$-$KMnO_4$ required) diluted with 200—400 ml of water. The solution is now heated to 80°—90° and at this temperature it is titrated with $\frac{N}{10}$-$KMnO_4$. In the neighborhood of the end point the beaker containing the liquid is removed for a short time from the sand bath in order to make manganese dioxide subside, and the colour of the liquid is observed. At the end point the colour of the solution becomes permanent for 2 or 3 minutes.

Experiment 1

Manganous ammonium phosphate used for analysis was prepared from 0.0625 grams of $(NH_4)_2HPO_4$, 1 ml of $MnCl_2$ solution, 25 ml of NH_4Cl solution, 0.3 ml of $NH_2OH \cdot HCl$ solution and 45 ml of water.

Water added	Sod. acetate	$\frac{N}{10}$-$KMnO_4$		P_2O_5		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
350	4.0	15.77	15.75	0.03357	53.71	−0.06
350	4.0	15.77	15.80	0.03367	53.88	+0.11
350	4.0	15.77	15.80	0.03367	53.88	+0.11

Experiment 2

The manganous ammonium phosphate used for this analysis was prepared from 0.03125 grams of $(NH_4)_2HPO_4$, 0.5 ml of $MnCl_2$ solution, 15 ml of NH_4Cl soiution, 0.2 ml of $NH_2OH \cdot HCl$ solution and 35 ml of water.

Water added	Sod. acetate	$\frac{N}{10}$-$KMnO_4$		P_2O_5		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
400	2.0	7.88	7.88	0.01679	53.77	±0.00
300	2.0	7.88	7.86	0.01675	53.60	−0.17
200	2.0	7.88	7.90	0.01684	53.88	+0.11

Experiment 3

The manganous ammonium phosphate used for analysis was prepared from 0.015625 grams of $(NH_4)_2HPO_4$, 0.3 ml $MnCl_2$ solution, 10 ml of NH_4Cl solution, 0.1 ml of $NH_2OH \cdot HCl$ solution and 30 ml of water. In this and the next experiment a micro-burette was used for titration.

Water added	Sod. acetate	$\frac{N}{10}$ $-KMnO_4$		P_2O_5		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
200	1.0	3.942	3.950	0.008418	53.88	+0.11
300	1.0	3.942	3.950	0.008418	53.88	+0.11
300	1.0	3.942	3.945	0.008408	53.81	+0.04

Experiment 4

The manganous ammonium phosphate used for analysis was formed from 0.0078125 grams of $(NH_4)_2HPO_4$, 0.2 ml of $MnCl_2$ solution, 5 ml of NH_4Cl solution, 0.1 ml of $NH_2OH \cdot HCl$ solution and 27 ml of water.

Water added	Sod. acetate	$\frac{N}{10}$ $-KMnO_4$		P_2O_5		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
200	1.0	1.971	1.975	0.004209	53.88	+0.11
200	1.0	1.971	1.968	0.004194	53.69	−0.08
200	1.0	1.971	1.968	0.004194	53.69	−0.08

Summary

1. Quantitative precipitation of phosphoric acid as $MnNH_4PO_4$ was made possible by the addition of a small quantity of hydroxylamine hydrochloride, and as a consequence, new methods for determining phosphoric acid both gravimetrically and volumetrically were established.
2. The appropriate quantities of manganous chloride and ammonium chloride to be taken for the precipitation of phosphoric acid were determined.
3. The influence of various salts such as sodium chloride, potassium

chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium citrate, ammonium tartrate and ammonium oxalate upon the precipitation were studied. The bad effect of ammonium molybdate and how to prevent it were carefully examined.

4. It was confirmed that the volumetric determination of manganese in manganous ammonium phosphate affords an excellent means for estimating minute quantities of phosphoric acid rapidly.

The writer wishes here to express his sincere thanks to Professor M. Matsui, at whose suggestion the work was carried out.

Quantitative Analysis of Phosphoric Acid, Part III. Determination as Zinc Ammonium Phosphate

By

Masayoshi Ishibashi

(Received October 30, 1928)

Since the method of precipitating zinc as zinc ammonium phosphate and determining it as the pyrophosphate was first proposed by H. Tamm[1] the investigation into this method has been undertaken by many authors[2]. As to the application of the reaction for determining phosphoric acid no investigation has yet been published, but judging from the analogy of zinc with magnesium and manganese such an application may be expected to be quite possible.

As the results of experiments carried out by the present writer it was made clear that the reaction of precipitating phosphoric acid as zinc ammonium phosphate can also be applied for determination of the acid, if strict care be paid regarding the acidity of the solution. The writer also tried to find some means by which zinc ammonium phosphate can be used for volumetric analysis of phosphoric acid, and found that the method[3] of estimating zinc in zinc ammonium phosphate indirectly by changing it first into the oxalate and titrating oxalic acid combined with

1 Chem. News **24**, 148 (1871); Zs. anal. Chem., **13**, 320 (1874).

2 G. Lösekann u. T. Meyer: Chem. Ztg., **10**, 729 (1886); Zs. anal. Chem., **26**, 78 (1887); T. Meyer u. M. Austin: Zs. anorg. Chem., **22**, 212 (1900); H. D. Dakin: Zs. anal. Chem., **39**, 273 (1900); K. Voigt: Ibid., **49**, 613 (1910); P. Artmann: Ibid., **54**, 89 (1915); **62**, 8 (1923); D. Balarew: Ibid., **60**, 442 (1921).

3 H. L. Ward: Amer. Jour. Sci., [4], **33**, 334; Gooch: Methods in Chemical Analysis p. 187 (1912).

zinc with potassium permanganate is applicable here and gives a tolerably good result, though the way may appear at first sight too roundabout.

Experimental

The following solutions were used in the experiments described below.
Phosphate solution.——10.0000 grams of Kahlbaum's ammonium phosphate "Zur Analyse mit Garantieschein" were dissolved in 1 litre.
Zinc chloride solution (about 1 molar).——136.3 grams of the salt were dissolved in water and diluted to 1 litre; white turbidity, if produced, was dissolved in dil. hydrochloric acid.
Ammonium chloride solution (about 5 molar).——A conc. solution containing 268 grams of the salt after having been made ammoniacal was left to stand for 2 or 3 days and then filtred. The filtrate was now made slightly acidic with hydrochloric acid and diluted to 1 litre.
Ammonia water.——About 2.5 % solution.

I. Gravimetric Method

After having conducted the experiment in many different ways the procedure described below was found to give the most satisfactory result in precipitating phosphoric acid as zinc ammonium phosphate. The important points are (1) the temperature at which precipitation takes place, (2) the acidity of the solution containing phosphoric acid, zinc chloride and ammonium chloride from which zinc ammonium phosphate is to be precipitated by addition of ammonia, (3) a constant agitation of the solution while precipitation is going on and (4) the acidity of the solution at the time when the precipitation is just completed.
Procedure.——To the phosphate solution an excess of zinc chloride and a still greater excess of ammonium chloride are added, and the acidity of this mixture is so regulated that either none or only a small quantity of zinc ammonium phosphate separates out at this point. The solution is then heated nearly to boiling point and well agitated till the amorphous precipitate completely changes into crystalline. Now ammonia water is slowly added while the mixture is well agitated, care being taken not to add the second drop before the precipitate formed by the first drop has become crystalline and also not to add more than to impart a slight yellow colour to p-nitrophenol previously added. As zinc ammonium phosphate is soluble both in acid and alkali it is of the utmost importance to restrict the acidity of the solution accurately. The P_H value of the

solution in which zinc ammonium phosphate is most insoluble was found to lie between 5—6.5 and such a point can be indicated by p-nitrophenol ($P_H = 5 - 7.9$; ammonia is added till a slightly yellow colour is produced), bromcresolpurple ($P_H = 5.2 - 6.8$; ammonia is added till an intermediate yellowish violet colour is produced) or neutral red ($P_H = 6.8 - 8.0$; ammonia is added till a slightly red colour, not a yellowish red colour, is produced). On cooling, the precipitate is filtered and washed with cold pure water, dried and ignited. For ignition a porcelein crucible is preferred, because zinc pyrophosphate often becomes fused when ignited in a platinum crucible.

It may be mentioned that the melting point of zinc pyrophosphate was determined to be 962° by the present writer.

Relation of Quantities of Phosphoric Acid, Zinc Choride and Ammonium Chloride to each other

In order to find out the suitable quantities of zinc chloride and ammonium chloride which should be taken for precipitation of zinc ammonium phosphate and also to learn the most suitable molecular relation between these two precipitants, a series of experiments were carried out, the results of which are shown in Table I.

It was shown in the preliminary experiment that the amount of zinc chloride does not much effect the accuracy of the analysis if other conditions are favourable. In the table this relation is shown quantitatively (No. 22—No. 26). All the other experiments from No. 1 to No. 21 were, therefore, carried out always with the molar ratio of zinc chloride to the phosphate maintained at 2.6.

The molar ratio of ammonium chloride to zinc chloride may be selected in a wide range, that is, between 50 and 100 without much effecting the result, as is seen in No. 1—No. 21. But the concentration of ammonium chloride has a more important bearing on the accuracy of the analysis. When the concentration is less than 2.0 Normal the value of phosphoric acid is found higher owing to the precipitation of normal zinc phosphate, $Zn_3(PO_4)_2$, whose presence in zinc pyrophosphate was proved by Tollen's reaction (No. 6—No. 8). If on the contrary its concentration is greater than 3.6 Normal it dissolves some zinc ammonium phosphate and consequently the result comes out somewhat lower (No. 13—No. 21).

Table I

For each experiment 25 ml of $(NH_4)_2HPO_4$ solution were taken.

No.	Water added	$ZnCl_2$			NH_4Cl			Time of standing	$Zn_2P_2O_7$	P_2O_5	Diff.	Phosphate in filtrate
	ml	ml	grm.	Mol. ratio to $(NH_4)_2HPO_4$	ml	grm.	Mol. ratio to $ZnCl_2$	hrs	grm.	%	%	
1	—	5	0.681	2.6	30	7.8	30	15	0.2879	53.68	−0.09	trace
2	100	„	„	„	„	„	„	„	0.3402	63.43	+9.66	none
3	—	„	„	„	50	13.4	50	„	0.2882	53.73	−0.04	none
4	—	„	„	„	„	„	„	„	0.2881	53.71	−0.06	none
5	20	„	„	„	„	„	„	10	0.2882	53.73	−0.04	none
6	50	„	„	„	„	„	„	10	0.2885	53.79	+0.02	none
7	100	„	„	„	„	„	„	10	0.2893	53.99	+0.22	none
8	200	„	„	„	„	„	„	10	0.2902	54.11	+0.34	none
9	—	„	„	„	60	14.1	60	15	0.2881	53.71	−0.06	none
10	30	„	„	„	„	„	„	10	0.2884	53.77	±0.00	none
11	50	„	„	„	„	„	„	10	0.2887	53.83	+0.06	none
12	100	„	„	„	„	„	„	10	0.2895	53.98	+0.21	none
13	—	„	„	„	75	19.6	75	15	0.2880	53.70	−0.07	none
14	50	„	„	„	„	„	„	15	0.2880	53.70	−0.07	none
15	—	„	„	„	100	26.8	100	15	0.2878	53.66	−0.11	trace
16	—	„	„	„	„	„	„	50	0.2877	53.64	−0.13	trace
17	50	„	„	„	„	„	„	20	0.2880	53.70	−0.07	trace
18	—	„	„	„	150	40.2	150	50	0.2874	53.59	−0.18	trace
19	100	„	„	„	„	„	„	50	0.2880	53.70	−0.07	trace
20	—	„	„	„	200	53.6	200	50	0.2860	53.43	−0.34	little
21	100	„	„	„	„	„	„	50	0.2881	53.71	−0.06	trace
22	—	3	0.409	1.6	30	7.8	50	15	0.2882	53.73	−0.04	none
23	—	5	0.681	2.6	50	13.4	50	15	0.2882	53.73	−0.04	none
24	—	10	1.363	5.3	100	26.8	50	15	0.2883	53.75	−0.02	none
25	—	20	2.726	10.6	200	53.6	50	15	0.2881	53.71	−0.06	none
26	100	20	2.726	10.6	200	53.6	50	15	0.2881	53.71	−0.06	none

Influence of various Salts present

The influence exerted by sodium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium tartrate, ammonium citrate and ammonium molybdate were examined and the results summarized in the following table were obtained.

Table II

For each experiment 25 ml of $(NH_4)_2HPO_4$ solution were taken.

No.	Salt mixed		$Zn_2P_2O_7$		P_2O_5	Diff.	Phosphate in filtrate
	Name	grm.	grm.	colour	%	%	
1	NaCl	3.0	0.2885	white	53.79	+0.02	none
2	$NaNO_3$	3.0	0.2884	white	53.77	±0.00	none
3	Na_2SO_4	1.0	0.2884	white	53.77	±0.00	none
4	„	2.0	0.2887	white	53.83	+0.06	none
5	$C_2H_3O_2Na$	4.0	0.2880	white	53.70	−0.07	trace
6	„	2.0	0.2883	white	53.75	−0.02	trace
7	KCl	4.0	0.3045	white	56.78	+3.01	none
8	„	2.0	0.2967	white	55.32	+1.55	none
9	Am. tartrate	2.5	0.2890	graiysh brack	53.88	+0.11	none
10	Am. citrate	2.5	0.2765	grayish brack	51.55	−2.22	none
11	Am. molybdate	2.4	0.2956	white	55.11	+1.34	little
12	„	1.2	0.2942	white	54.85	+1.08	little

$NaCl$, $NaNO_3$, Na_2SO_4.——No influence (No. 1—No. 4).

$C_2H_3O_2Na$.——It makes the precipitation of phosphoric acid somewhat incomplete, trace of it being left in the filtrate (No. 5—No. 6).

KCl.——Some zinc potassium phosphate is formed together with zinc ammonium phosphate, so that the precipitate fuses more easily when ignited, and the ignited residue shows Tollen's reaction. This bad effect can be got rid of to a certain degree by double precipitation (No. 7—No. 8).

Ammonium tartrate.——This is adsorbed in the precipitate of zinc ammonium phosphate, but can be easily taken off by double precipitation.

Ammonium citrate.——Its effect is rather curious. Though it does not interfere with the precipitation of zinc ammonium phosphate, it causes a

remarkably great negative error (No. 10). By repeating precipitation twice this bad effect may also be avoided.

Ammonium molybdate.——Accurate determination of phosphoric acid in the presence of molybdate is impossible, as the bad effect of the latter can not be prevented in any of the usual ways.

II. Volumetric Method

Indirect determination of phosphoric acid by titrating zinc in zinc ammonium phosphate was attempted. Of all the volumetric methods for determining zinc hitherto known, only H. L. Ward's oxalate method[1] was found to give fairly good results, though it may be felt too indirect to be applied for the determination of phosphoric acid.

Experiment 1.——Zinc ammonium phosphate was precipitated from a solution consisting of 25 ml of ammonium phosphate solution (0.2500 grm. of $(NH_4)_2HPO_4$), 5 ml of zinc chloride solution and 50 ml of ammonium chloride solution according to the procedure described before. The precipitate was filtered after a night's standing and well washed with cold water, and then converted into zinc oxalate by treating it with oxalic acid. After adding some sodium acetate and glacial acetic acid the solution in which zinc oxalate is precipitated was heated for a few minutes nearly to boiling point and left to stand for about 3 hours. Zinc oxalate was now filtered with a glass filter, washed several times with a small quantity of water and dissolved in hot dil. sulphuric acid. The sulphuric acid solution thus obtained was warmed in a water bath and titrated with $\frac{N}{10}-KMnO_4$.

$\begin{matrix}COOH\\ \vert\\ COOH\end{matrix}$	CH_3COOH (glacial)	$\frac{N}{10}-KMnO_4$ (ml)		P_2O_5	Diff.
grm.	ml	calc.	found	%	%
2.0	60	37.84	37.85	53.76	−0.01
3.0	100	37.84	37.82	53.73	−0.04
3.0	100	37.84	37.84	53.77	±0.00

Experiment 2.——25 ml of the solution containing 0.1250grm. of ammonium phosphate, 3 ml of zinc chloride solution and 30 ml of ammonium chloride solution were used for precipitation of zinc ammonium phosphate.

1 Loc. cit.

COOH | COOH	CH_3COOH (glacial)	$\frac{N}{10}-KMnO_4$ (ml)		P_2O_5	Diff.
grm.	ml	calc.	found	%	%
1.5	50	18.92	18.85	53.57	−0.20
2.0	60	18.92	18.87	53.62	−0.15
2.0	60	18.92	19.00	53.99	+0.22

Experiment 3.——25 ml of the solution containing 0.0625 grm. of ammonium phosphate, 1.3 ml of zinc chloride solution and 15 ml of ammonium chloride solution were employed. In this experiment a micro-burette was used for titration.

COOH | COOH	CH_3COOH (glacial)	$\frac{N}{10}-KMnO_4$ (ml)		P_2O_5	Diff.
grm.	ml	calc.	found	%	%
1.5	50	9.461	9.470	53.82	+0.05
1.0	50	9.461	9.450	53.71	−0.06
1.0	50	9.461	9.480	53.88	+0.11

Summary

1. A new gravimetric method for determining phosphoric acid as zinc pyrophosphate was established.

2. The most favourable relation between the quantities of zinc chloride and ammonium chloride which are to be taken for precipitation of phosphoric acid and also their relation to the amount of phosphoric acid taken for analysis were studied.

3. The hydrogen ion concentration of the solution necessary for the complete precipitation of zinc ammonium phosphate was determined.

4. The influence of various salts such as sodium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium tartrate, ammonium citrate and ammonium molybdate was examined.

5. It was also confirmed that with fairly good results phosphoric acid may indirectly determined by titrating zinc in zinc ammonium phosphate according to the oxalate method of H. L. Ward.

The writer wishes here to express his sincere thanks to Professor M. Matsui under whose kind guidance and encouragement the work was carried out.

The Anodic Behaviour of Substituted Acetic Acids, Part I. Diphenylacetic Acid

By

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and
Motooki Matsui

(Received November 27, 1928)

As is well known, the anodic behaviour of fatty acids is not always the same; some change chiefly to hydrocarbon, saturated or unsaturated, while others are transformed into esters or alcohols. The property of an acid undergoing such an electrolytic reaction, called the Kolbe reaction, becomes greatly modified when hydrogen in the alkyl radical is substituted by other radicals. For example, mono-, di- and tri-chloracetic acids differ from each other and also from acetic acid itself in their anodic reaction.

To see how the anodic reaction of acetic acid is effected by a phenyl radical, diphenylacetic acid was electrolyzed with direct and alternating current and the results described below were obtained.

I. Electrolysis with Direct Current

A fifty per cent solution of potassium diphenylacetate acidified with a drop of sulphuric acid was first electrolyzed in a bath provided with a diaphragm, by passing a current of 45 amperes per 100 sq. cm. at a temperature of below 30° for an hour. As there was produced no synthesized substance, the electrolysis was renewed with a bath having no diaphragm, into which a current of air free from carbon dioxide was passed, in order to drive off carbon dioxide formed in the electrolysis (see Fig. 1). Both electrodes consisted of similar platinum spirals and the temperature of the bath was kept below 38° by cooling with a freezing mixture.

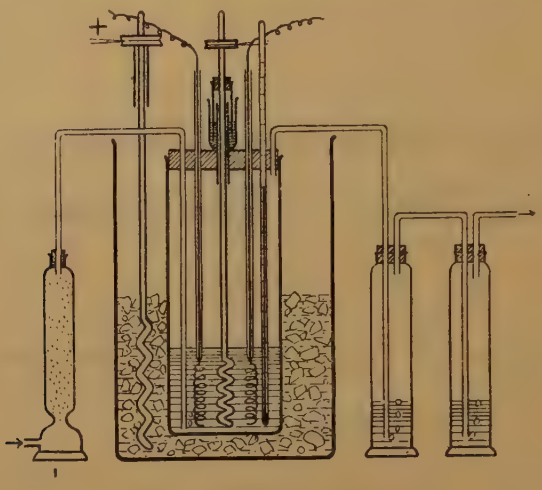

Fig. 1

After a current of 55 amperes per 100 sq. cm. had been passed for 15 hours, about 3.3 grams of a reaction-product consisting of diphenyl methyl alcohol (98%) and diphenylacetic diphenylmethyl ester (2%) were obtained. When lead was used as the cathode the yield of the alcohol, but not the ester, was increased to more than 3 times. This is no doubt due to the catalytic action of lead, for the same result may also be obtained with a platinum cathode, if some lead oxide is added to the bath.

The influence of external conditions on the electrolytic reaction was examined by measuring carbon dioxide evolved from the bath, on the assumption that the whole of the carbon dioxide is produced only by the Kolbe reaction.

(*a*) *Influence of the Concentration of the Electrolytic Solution*

Current density, 55 amp/100 sq. cm.; temperature, 25°

Conc. of solution (%)	CO_2
20	not evolved
35	very little
50	much evolved

(*b*) *Influence of Current Density*

Sixty grams of 55% potassium diphenylacetate solution were electrolyzed for 4 hours.

Current density (amp./100 sq. cm.)	Temp.	CO_2 (gram)
2	0°	0
4	4°	0.008
20	20°	0.13
30	29°	0.25
55	39°	0.57

(*c*) *Influence of Acidity of the Solution*

Concentration of the solution, 55%; temperature, 29°; current density, 55 amp/100 sq. cm.

Acidity of solution	Time (hours)	CO_2 (gram)
Neutral	3	0
Acidified with diphenyl acetic acid	3	0
A drop of H_2SO_4 added	3	0.41
A drop of HCl „	3	0.22

From the results above stated it is seen (1) that the Kolbe reaction of diphenyl acetic acid does not take place with a solution more diluted than 20%; (2) that evolution of carbon dioxide is increased when current density increases, and as long as current density is kept below 4 amp/100 sq. cm. no appreciable amount of carbon dioxide is evolved; (3) that neither a neutral solution nor a solution made acidic with diphenyl acetic acid undergoes the Kolbe reaction, the solution acidified with a drop of sulphuric acid giving off carbon dioxide most abundantly.

II. Electrolysis with Alternating Current

In the electrolysis of diphenyl acetic acid, as it was found difficult to pass a direct current of high density maintaining at the same time

the temperature of the bath low, electrolysis with an alternating current in a bath having no diaphragm was undertaken, on the presumption that diphenyl acetic acid, as well as the substances which would be formed from it at the anode, would cathodically be inactive. Twenty grams of 50% potassium diphenyl acetate solution acidified with a drop of sulphuric acid were put in a U-tube cooled with a freezing mixture, and from both sides of the tube platinum spirals were inserted as the electrodes. Now an alternating current of about 3 amperes (90 am/100 sq. cm.) was passed for an hour, the temperature of the bath being kept sometimes at 10° and sometimes at 25°. During the electrolysis carbon dioxide was evolved from both electrodes, and some crystalline substance separated out. The electrolytic solution became coloured dark brown and showed a fairly strong alkaline reaction at the end of the electrolysis (see Fig. 2).

Now the crystalline substance formed by electrolysis was separated by filtration, washed well with water and recrystallized from alcohol. It crystallized in prismatic form and melted at 106°. The yield was about 1.5 grams. The results of analysis and of molecular weight determination showed it to be diphenylacetic diphenyl methyl ester.

0.1014 g taken for analysis gave 0.3181 g CO_2 and 0.0546 g H_2O. C=85.57%, H=5.98% (calc. C=85.68%, H=5.86%).

The molecular weight was determined by the cryocospic method using 16.25 grams of benzene as the solvent.

Substance taken 0.2126 g, depression of freezing point 0.176°, mol. wt. 372 (calc. 378).

It was also confirmed that the substance changes into diphenylacetic acid and diphenylmethyl alcohol, when saponified with 20% alcoholic potash solution.

The filtrate separated from the ester above stated was neutralized with dilute sulphuric acid and distilled with steam, when about 2 grams of a substance crystallizing in long needles were obtained. It melted at 65.5° and boiled at 298°. Its acetyl value was determined by acetylating 0.6444 gram of it.

Acetic anhydride required, 0.00351 mol. (calc. 0.00350). The substance was thus proved to be diphenylmethyl alcohol.

As the relation between the amount of the ester and of the alcohol produced by the direct current was seen to differ from that produced by the alternating current, experiments were performed to determine the difference definitely by electrolyzing 50% potassium diphenyl acetate solution with the current of 55 amp./100 sq. cm. at about 25°. In the case

of the direct current, about 3.2 grams of diphenylmethyl alcohol and 0.08 gram of diphenylacetic diphenylmethyl ester were produced after 15 hours' electrolysis, while with the alternating current, 0.1 gram of the alcohol and 1.0 gram of the ester were obtained after passing the current for an hour.

It might at first be conjectured that either one of the above two substances would be the primary product formed electrolytically and the other the secondary one derived from the former purely chemically. Such a conjecture was, however, proved to be quite groundless by the following two experiments.

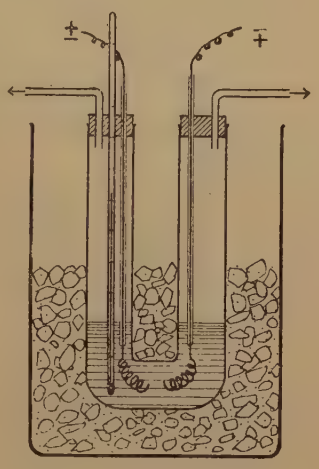

Fig. 2

Experiment 1.—Diphenylacetic diphenylmethyl ester was added to a concentrated caustic potash solution, and this solution was electrolyzed with a direct current of 80 amp./100 sq. cm. at 50°. Even after 10 hours' electrolysis no diphenyl methyl alcohol was yielded.

Experiment 2.—Diphenylmethyl alcohol was added to 10% potassium diphenylacetate solution and after the solution had been made faintly alkaline with caustic potash an alternating current was passed through it under conditions similar to those used for the electrolysis before described. But no ester could be obtained.

From the experimental facts so far observed, it may be concluded that the concentrated solution of potassium diphenylacetate undergoes the anodic reaction so as to yield diphenylacetic diphenylmethyl ester and diphenylmethyl alcohol which seem to be produced each independently from the other. The reason why the formation of diphenylmethyl alcohol predominates when the direct current is used, will not be difficult to understood if we admit that, in the course of electrolysis, hydroxylion in the neighborhod of the anode may possibly take such a concentration as is favourable to the formation of alcohols, even though the electrolytic solution is in vigorous agitation. As is generally known, neither a strongly alkaline solution nor an acidic solution is suitable for the formation of alcohol.

This investigation will be extended to other substituted acetic acids.

Summary

1. The Kolbe reaction of potassium diphenylacetate was studied using direct as well as alternating current.

2. With the alternating current, the electrolytic reaction took place far more readily and produced diphenylacetic diphenylmethyl ester and diphenylmethyl alcohol, the amounts of which were found to differ from those produced with the direct current.

3. Experiments were conducted to see if one of the two products—ester and alcohol—is not the secondary one formed from the other purely chemically,

4. It was found that the use of an alternating current is preferable, when the substance to be electrolyzed and also the synthesized product are not reducible.

Organic Compounds of Arsenic, Part VI. Electrolytic Reduction of Some Aryl-Arsinic Acids

By

Kaoru Matsumiya and **Hisakazu Nakata**

(Received December 26, 1928)

In our previous work[1] on the electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid, it was shown that the cathode material and the strength of the acid in the cathode solution have remarkable effects on the final products of electrolysis. The cathode materials used were then limited to mercury, lead and lead amalgam; we have therefore continued the work further to see the effects of platinum, nickel and copper when used as the cathode.

It is already known that arsenic and arsinic acids are not reduced in an alkaline medium[2]. In an acidic medium, however, it was found, as stated below, that arsinic acid radical is also practically not reducible when cathodes of lower over-voltage are used. In fact, with the cathode of platinum, nickel or copper, the reduction of 3-nitro-4-hydroxyphenylarsinic acid takes place only in the nitro group, there being formed 3-amino-4-hydroxyphenylarsinic acid and 3,3′-azoxy-4,4′-dihydroxyphenyl-1,1′-diarsinic acid. Similarly, 3,4-diaminophenylarsinic acid is obtained as the reduction product from 3-nitro-4-aminophenylarsinic acid.

The concentration of the acid exerts on the reduction of 3-nitro-4-hydroxyphenylarsinic acid[3] such an influence that in a dilute hydrochloric acid solution it goes on directly to the arsine stage, while at a higher concentration it remains only in the state of the arseno-compound. To

1 These memoirs, **10**, 199 (1926)
2 Covelli: Chem. Ztg., **33**, 1209 (1909);
F. Fichter and E. Elkind: Ber., **49** 239 (1916)
3 Our previous paper, loc. cit.

see whether the same influence is observed with the other arsinic acids, experiments were undertaken with 4-aminophenylarsinic acid and 4-hydroxyphenylarsinic acid.

According to Fr. Fichter and E. Elkind[1] 4-aminophenylarsinic acid is reduced to 4-aminophenylarsine with dilute hydrochloric acid, but with the acid more concentrated than 2-N, the hydrochloride of 4-aminophenylarsine, which is insolube in concentrated hydrochloric acid, covers the surface of the cathode and hinders the further progress of reduction. In our experiments with 4-aminophenylarsinic acid in concentrated hydrochloric acid solution a similar result to that in the case of 3-nitro-4-hydroxyphenylarsinic acid was obtained, p-arsenoaniline being its reduction product. We could also prepare 4-hydroxyphenylarsine and 4,4′-dihydroxyarsenobenzene from 4-hydroxyphenylarsinic acid in a similar manner by changing the acidity of the catholyte.

The limit of concentration of the acid beyond which the reduction product changes from arsine to arsenocompound is not always the same; it is 4.7-N for 3-amino-4-hydroxyphenylarsine and 3,3′-diamino-4,4′-dihydroxyarsenobenzene, 8-N for 4-aminophenylarsine and 4,4′-diaminoarsenobenzene, and 4-N for 4-hydroxyphenylarsine and 4,4′-dihydroxyarsenobenzene. Perhaps this property may be utilized as a convenient, electrolytical method for preparing various arseno-compounds from the corresponding arsinic acids.

Experimental Part

1) Reduction of 3-nitro-4-hydroxyphenylarsinic acid with platinum, nickel and copper cathodes

A patent process[2] is known for preparing aminoxyphenylarsinic acid by electrolyzing 3-nitro-4-hydroxyphenylarsinic acid in an alkaline solution. We have, however, found that an acid solution may also be used for the same purpose in the following manner:—

The cathode solution was prepared by dissolving 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid in 125 c.c. of 2.5-N HCl and into this solution a platinum plate (4 × 10 cm.) was dipped as cathode. When a current of 2 amps. was passed at 25°, the cathode solution soon became brown and

1 loc. cit.

2 U. S. P., 1232373

the yellow precipitate of azoxyphenoldiarsinic acid began to separate. The solution was vigorously stirred during the electrolysis in order to prevent the cathode from being covered with the precipitate. After 80 minutes the current was cut off; the yellow precipitate was separated by filtering and dried in a desiccator. To the filtrate 45 grms. of sodium acetate was added, by which 3-amino-4-hydroxyphenylarsinic acid was separated in a brown crude state.

3,3′-azoxy-4,4′-dihydroxyphenyl-1, 1′-diarsinic acid is a yellow, fine needle crystal which darkens at about 210° and gradually decomposes without melting. It is soluble in hot water, methyl and ethyl alcohol; sparingly so in cold water and dilute mineral acids; and insoluble in acetone, ether, benzene, chloroform and carbon bisulphide. Its aqueous solution has an acid reaction on litmus. When treated with zinc dust, its alkaline solution becomes by and by colourless, and this colourless solution shows a power of reducing ammoniacal silver nitrate, while the original acid does not.

It was recrystallized from hot water and analysed with the following result:—

0.0988 grms. subst. required 15.20 c.c. of N/10 iodine soln.

0.1313 grms. subst. gave 0.1450 grms. CO_2 and 0.0327 grms. H_2O.

	found	calc. for $C_{12}H_{12}O_6N_2As_2$
C	30.13%	30.14%
H	2.78%	2.53%
As	31.31%	31.36%

To purify the crude aminoxyphenylarsinic acid obtained by the above method, it was dissolved in dil. HCl, decolourized with animal charcoal and recrystallized from a solution containing sodium acetate. It darkens at 170° and decomposes gradually. Its dil. HCl-solution assumes a deep red colour on the addition of one drop of potassium bichromate solution, which is the characteristic property of the aminoxyphenylarsinic acid.

0.1860 grms. subst. required 15.20 c.c. of N/10 iodine soln.

	found	calc. for $C_6H_8O_4NAs.\frac{1}{2}H_2O$
As	30.65%	30.97%

The acid acetylated with acetic anhydride was also analysed.

0.1665 grms. subst. required 12.00 c.c. of N/10 iodine soln.

	found	calc. for $C_8H_{10}O_5NAs$
As	27.03%	27.25%

When working with a nickel or a copper cathode, we could also observe the presence of a compound other than the above-mentioned,

though it could not be isolated on account of its being too small in quantity. From the properties of the compound in solution, however, it may certainly be inferred that the arsinic acid radical must have undergone reduction.

The relation between the amounts of the reduction-products and cathode material is as follows :—

Anode :	carbon
Catholyte :	2 grms. 3-nitro-4-hydroxyphenylarsinic acid in 125 c.c. 2.5-N HCl
Anolyte :	2.5-N HCl
Current :	2 amps.
Time :	1 1/3 hours.
Temperature :	25°

Cathode (4×10 sq. cm.)	Azoxyphenoldiarsinic acid (grm.)	Aminoxyphenylarsinic acid (grm.)
copper	0.25	1.05
nickel	0.46	0.72
platinum	0.70	0.62

2) Reduction of 3-nitro-4-aminophenylarsinic acid with copper cathode

The cathode solution was prepared by dissolving 5 grms. of 3-nitro-4-aminophenylarsinic acid in a mixture of 30 c.c. of HCl (D. 1.19), 90 c.c. of methyl alcohol and 10 c.c. of water. Taking a copper plate (5 × 10 cm.) as the cathode, a current of 1 amp. was passed at 28–30° for 6 hours, the cathode solution becoming brownish during the electrolysis. After evaporating methyl alcohol at a reduced pressure the cathode solution was carefully neutralized with sodium hydroxide, when 3, 4-diaminophenylarsinic acid separated out as chocolate-brown crystals. It was decolourised with animal charcoal and recrystallized from hot water. It crystallizes in colourless, minute needles which darken at 140° and melt, with decomposition, at 158°. Its dil. HCl-solution produces a deep violet colour with potassium bichromate solution. The yield was about 70 per cent.

0.1630 grms. subst. required 13.45 c.c. of N/10 iodine soln.

	found	calc. for $C_6H_3O_3N_2As.\ \frac{1}{2}H_2O$
As	30.95%	31.09%

3) Reduction of 4-aminophenylarsinic acid.

a) Preparation of p-arsenoaniline

The apparatus was the same as shown in the previous paper[1]; all the experiments were carried in a carbon dioxide atmosphere.

Five grms. of 4-aminophenylarsinic acid dissolved in 50 c.c. of 11-N HCl were reduced at the mercury cathode (28 sq. cm.) by a current of 1 amp., the temperature being kept at 25°. After the electrolysis the yellow precipitate of 4,4′-arsenoaniline dihydrochloride was separated by filtration and dried in vacuo over sodium hydroxide. The yield was 55 per cent.

0.2185 grms. subst. required 20.48 c.c. of N/10 iodine soln.

	found	calc. for $C_{12}H_{14}N_2As_2Cl_2.H_2O$.
As	35.18%	35.27%

b) Influence of the strength of acid

Cathode:	mercury
Anode:	carbon
Catholyte;	3 grms. 4-aminophenylarsinic acid in 60 c.c. of HCl
Anolyte:	HCl of the same strength as the catholyte
Current:	1 amp.
Temperature:	25–30°

Normality of acid	Aminophenylarsine hydrochloride (grm.)	Arsenoaniline dihydrochloride (grm.)
3	2.1	0
6	1.7	0
8	0.1	0.6
10	0	1.2

1 loc. cit.

4) Reduction of 4-hydroxyphenylarsinic acid

a) Preparation of 4-hydroxyphenylarsine

Four grms. of 4-hydroxyphenylarsinic acid dissolved in 100 c.c. of 1-N HCl were reduced by means of a mercury cathode with a current of 1 amp. the temperature being kept at 25–30°. After electrolysis for 5 hours the whole cathode solution, which contained some yellowish precipitates, was made alkaline with sodium hydroxide, through which carbon dioxide gas was passed, whereupon slightly yellow coloured needle crystals of 4-hydroxyphenylarsine separated out. It was filtered and dried; the yield was 48 per cent. It becomes reddish at 75° and decomposes completely at 155°.

0.1446 grms. subst. required 16.80 c.c. of N/10 iodine soln.

	found	calc. for C_6H_7OAs
As	43.57%	44.07%

b) Preparation of p-arsenophenol

The cathode solution was prepared by disssolving 5 grms. of 4-hydroxyphenylarsinic acid in 100 c.c. of 6-N HCl and was subjected to electrolytic reduction under conditions similar to those in the previous experiment. After 4 hours the current was cut off and the brown precipitate of p-arsenophenol was separated. It was purified by reprecipitation with carbon dioxide gas from its alkaline solution. The yield was 60 per cent. It is a yellowish brown powder which darkens and decomposes at 200°.

0.1321 grms. subst. required 15.80 c.c. of N/10 iodine soln.

	found	calc. for $C_{12}H_{10}O_2As_2$
As	44.85%	44.61%

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On the Electrolytic Reduction of Aldehydes, Part V. Cinnamic Aldehyde

By

Goro Shima

(Received December 19, 1928)

The electrolytic reduction of cinnamic aldehyde was tried by Law[1] who reported that the aldehyde undergoes reduction neither in an acid nor in an alkaline solution, but changes to a resinous substance. By using a neutral solution, however, he succeeded in obtaining phenyl propyl alcohol with 55% yield. As the neutral catholyte he took a mixture[2] of water, alcohol, ethyl acetate and potassium acetate, in which ethyl acetate plays the part of using up alkali as it is formed. T. Shimamoto[3] also undertook to reduce the aldehyde in a sulphuric acid solution as well as in a neutral solution using platinum, lead or mercury as the cathode. The results obtained by him were always unsatisfactory, the yield of phenyl propyl alcohol having been not more than 10% even in the neutral solution. As I had, by using a sodium bicarbonate solution as the catholyte, succeeded in reducing oxybenzaldehydes[4], vanillin and piperonal[5] with the good yields of 80—90%, it was now attempted to see whether the same catholyte would not be similarly effective in the reduction of cinnamic aldehyde. When an electrode having a great over-voltage like mercury was used in a neutral catholyte the reduction of the double bond and of the aldehyde group took place simultaneously, and phenyl propyl alcohol was produced with the yield of more than 70%. Electrodes with

1 Jour. Chem. Soc., **89**, 1512 (1906); **99**, 1113 (1911); **101**, 1016 (1912).
2 Elbs, Ber., **38**, 4012 (1905).
3 The work is not yet published.
4 These Memoirs, **11**,. 407 (1928).
5 Ibid, **11**, 419 (1928).

a smaller over-voltage, such as platinum, nickel and copper only resinized the aldehyde, no corrresponding alcohol being formed. I also traced Law's experiment with a neutral solution and found the yield of phenyl propyl alcohol to be far lower than Law stated, when lead was used as the cathode. The yield was increased to 50% by substituting mercury for lead as the cathode.

In the reduction of vanillin and piperonal[1] it was observed that their reduction to the corresponding alcohols is rather hindered when alcohol is taken as their solvent, while in the case of cinnamic aldehyde the presence of a suitable quantity of alcohol in the cathode solution favours the reduction, though its excess has the contrary effect.

Experimental

1. Electrolytic Reduction in a Sodium Bicarbonate Solution

The apparatus used for the experiment was similar to that previously employed for the reduction of oxyaldehydes[2]. As the cathode solution, a saturated sodium bicarbonate solution mixed with some dilute alcohol was taken and into this solution a current of carbon dioxide was passed constantly during the electrolysis. Five grams of cinnamic aldehyde used for each experiment, were added drop by drop to the cathode solution, which was always vigorously agitated. Mercury was used as the cathode and a platinum plate as the anode. The latter was dipped in the anode solution consisting of 5% caustic soda solution.

After the electrolysis was over the cathode solution was diluted with much water and extracted with ether. The residue after evaporating the ether from the ether extract was subjected to steam distillation, and the distillate was treated with sodium bisulphite in order to fix the aldehyde remaining unchanged. Phenyl propyl alcohol was now extracted with ether, dehydrated and purified by distillation. It is a thick colourless liquid having an agreeable odour. Its boiling point was found to be 235° at ordinary pressure, 120° by 12 mm and 115° at 8 mm pressure.

0.1003 g substance: 0.2914 g CO_2 and 0.0794 g H_2O,
C=79.25%, H=8.86%; Calc. C=79.35%, H=8.89%

A residue having a gummy consistency was obtained after steam distillation. It was soluble in ether and did not crystallize even when left to

1 Loc. cit.
2 Loc. cit.

stand for several months.

The results of electrolysis under different conditions are shown in the following table.

Table I

No.	Temperature	Catholyte cc		Current density	Current quantity	Phenyl propyl alcohol	Residue
		Alcohol	Bicarbonate sol.	amp/100 sq. cm.	amp-hour	%	%
1	25°–28°	—	100	10.0	4.0	16	8
2	20°–25°	30	80	7.5	14.0	56	20
3	20°–22°	40	60	7.5	12.0	60	20
4	25°–30°	40	60	7.5	13.5	56	24
5	10°–15°	50	50	6.0	11.5	42	20
6	20°–25°	50	50	6.0	10.0	58	22
7	25°–28°	70	50	10.0	4.0	38	22
8	25°–30°	70	50	18.0	8.0	36	52
9	25°–27°	70	50	9.0	8.0	42	34
10	18°–22°	70	50	5.0	7.0	44	46
11	15°–18°	70	50	4.0	8.0	40	46
12	20°–22°	70	50	6.0	12.0	72	14
13	27°–30°	70	50	7.5	12.0	68	16
14	25°–30°	70	30	7.5	10.0	50	36

When the results shown in No. 1 and No. 7 are compared it is cleary seen that the addition of alcohol to the cathode solution greatly favours the reduction though its presence in amounts of more than 60% acts contrarily by accelerating the polymerization of the aldehyde (compare with No. 14). Both high temperature and great current density tend to increase polymerization; perhaps the temperature of 15°–20° and current density of 5—10 amperes per 100 sp. cm. are the most favourable. In the experiments from No. 7. to No. 11, 5 grams of the aldehyde were added to the cathode solution at the commencement of the reaction all at once, and as a natural consequence of this the formation of the resinous matter was greatly increased. In order to prepare phenyl propyl alcohol with a good yield it is very important to add the aldehyde drop by drop at such a rate that the second portion drops in after the first portion

has undergone reduction.

2. Electrolytic Reduction in an Alcoholic Ethyl Acetate Solution

Cathode solution : 20 cc. of ethyl acetate + 20 cc. of alcohol + 20 cc. of water + 4 gr. of potassium acetate + 5 gr of cinnamic aldehyde.
Current density : 6 amp./100 sq. cm.
Anode : Platinum plate
Anode solution : 5 % caustic potash solution

As the cathode, well purified lead or mercury was used, and the cathode solution was strongly stirred. With the cathode of lead the yield of phenyl propyl alcohol could not be raised to more than 24 %, while with the mercury cathode a 50% yield was procured.

Table II

No.	Cathode	Temperature	Current quantity amp.-hour	Phenyl propyl alcohol %	Resinous matter %
1	Pb	20°—22°	6	24	54
2	Hg	20°—22°	6	48	34
3	Hg	25°—30°	8	50	36

The electrolysis was also conducted in the cathode solution chiefly consisting of 60% acetic acid with different cathodes, but in no case phenyl propyl alcohol was produced.

In conclusion, the writer wishes to express his sincere thanks to Professor M. Matsui for his kind guidance and encouragement throughout this research.

On the Electrolytic Reduction of Aldehydes, Part VI. Complete Reduction of the Carbonyl Group

By

Goro Shima

(Received December 20, 1928)

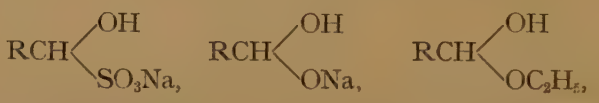
Though an aldehyde is reducible electrolytically to the corresponding alcohol and pinacone with ease, its complete reduction to hydrocarbon can only be brought about under some specific conditions. Tafel and Schepss[1] found that both aldehyde and ketone are best reduced to hydrocarbon when cadmium is used as the cathode. Since that time cadmium has been regarded as the only cathode which can be used for complete reduction of the carbonyl group. Inferring from the close analogy existing between cadmium and zinc, and from the fact that zinc acts chemically as such an effective reducing agent that it is practically employed universally in many chemical reductions, and that its over-voltage for evolving hydrogen is notably higher than that of cadmium, it is conceivable that a zinc cathode will give rise to the formation of hydrocarbon with an efficiency perhaps surpassing that of cadmium or at least similar to it.

To verify this experimentally I undertook the electrolytic reduction of anisaldehyde, salicylaldehyde, paraoxybenzaldehyde, vanillin and piperonal, and observed that the formation of hydrocarbons was always greater at the zinc cathode than at the cadmium. Especially salicylaldehyde which does not change to the corresponding cresol when reduced with the latter elect-

1 Ber., **41**, 2148 (1911); Schepss, Ber., **46**, 2566 (1913), Tafel, Ber., **42**, 3146 (1909).

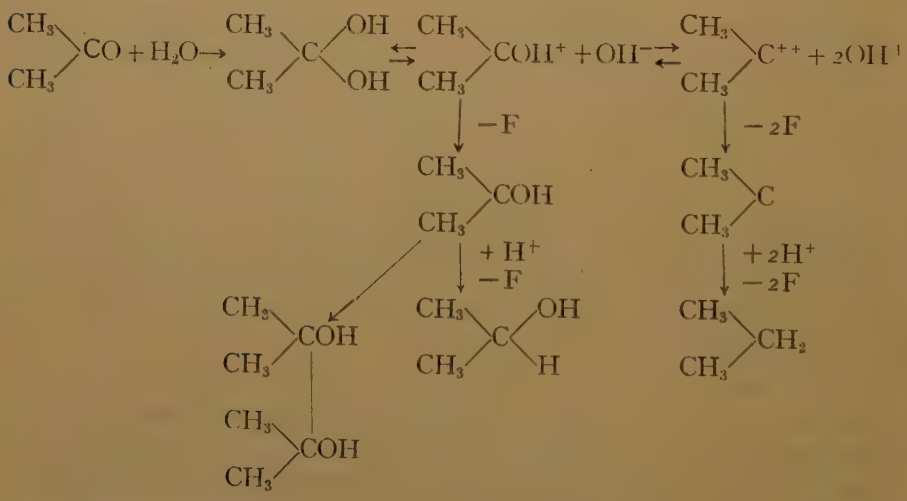
rode could at the former electrode be transformed into it with 65% yield.

As I have frequently observed, the presence of alcohol in a large quantity effects the electrolytic reduction of aldehyde in such a way as to lead to the formation of condensation-products such as pinacone or still more complicated resinous matter, thus preventing the formation of simple reduction-products like alcohol and hydrocarbon. As a most typical example of this the reduction of vanillin may be mentioned here. While vanillin is reduced in a sulphuric acid solution to o-creosol with 75 % yield, the same reduction can scarcely be observed when the cathode solution containing much alcohol is electrolysed. The electrolytic reduction of aldehyde and ketone in acid sodium sulphite solutions[1] and also that of aldehyde in caustic soda solutions[2] generally take place in a preicsely similar manner chiefly producing condensation-products. Perhaps these reactions may be regarded as belonging to the same kind of reduction, that is, reduction of the addition-products of aldehyde or ketone such as



which naturally differs from that of free aldehyde or ketone.

Erich Müller[3] tried to explain the reduction of aldehyde and ketone, representing its progress in the following scheme:



1 Kauffmann, Z. Elektrochem., **2**, 1265 (1896); **4**, 361 (1898).
2 Law, J. Chem. Soc., **89**, 4512 (1906).
3 Z. angew. Chem., **35**, 698 (1922).

Ingenious as it is, Muller's theory seems still insufficient to explain the above-stated difference existing between the electrolytic behaviour of aldehyde and of its addition-products.

Experimental

Into a glass cylinder having a diameter of 6 cm. which was used as the anode chamber, a cell of about 200 cc. capacity (diameter, 4.5 cm.) was placed as the cathode compartment. Zinc amalgam used as the cathode was prepared by electrolysing a concentrated solution of zinc sulphate till mercury taken as the cathode solidified completely. The cathode solution consisted of sulphuric acid of different dilution or of alcoholic sulphuric acid into which 5 grams of aldehyde to be reduced were added little by little on vigorous agitation. A platinum plate was dipped as the anode in 30 % sulphuric acid contained in the cell.

1. Anisaldehyde

By electrolyzing anisaldehyde in 5 % alcoholic sulphuric acid solution with a copper cathode, Law[1] obtained anisic alcohol (70–75%) and p-methyl anisole (5%). Tafel and Schepss[2] used cadmium in place of copper and by this means raised the yield of p-methyl anisole to 37%. Examining the influence of the temperature, current density and concentration of the sulphuric acid in the cathode solution the latter authors determined the best conditions for the production of p-tolyl methyl ether and working under those conditions a 60 % yield was finally procured. The conditions they used were: Anode solution—20 gm. of anisaldehyde + 60 c.c. of water + alcohol to 180 c.c + 15 gm. of conc. sulphuric acid; Temperature —below 25°; Current density—30 amp./100 sq. cm.

I conducted a series of experiments to reduce anisaldehyde to p-tolyl methyl ether using zinc amalgam as the cathode. The cathode solution after electrolysis was diluted with much water and treated with ether in order to extract the substances dissolved in it. To the ether extract, calcium chloride was added to remove alcohol and water from it, and after the ether had been evaporated off, it was distilled under reduced pressure. The portion distilling at 66°–70° at 14 mm. pressure was collected. It boiled at 175° at ordinary pressure. It was analysed with

1 J. Chem. Soc., **91**, 748 (1907).

2 Loc. cit.

the following results:

0.1416 gm. substance gave 0.4065 g CO_2 and 0.1039 g H_2O,
C=78.29%, H=8.20%; Calc. C=78.69%, H=8.20%

The results of experiments conducted under various conditions are given thus:

Table I

No.	Catholyte			Current density amp./100 sq. cm.	Current quantity amp.-hour	Temperature °C	p-Tolyl methylether %
	Sulphuric acid		Alcohol cc				
	%	cc					
1	30	80	—	36	18	20–25	10
2	50	80	—	48	20	20–25	30
3	60	80	—	30	17	15–25	39
4	60	80	—	36	18	20–25	40
5	60	80	—	36	18	30–35	31
6	60	80	—	48	20	20–25	38
7	60	80	—	60	25	30–35	32
8	70	80	—	30	30	12–16	51
9	70	80	—	36	30	12–20	45
10	70	80	—	48	28	23–28	40
11	70	80	—	48	25	20–25	43
12	80	80	—	30	20	20–25	5
13	40	50	30	30	15	12–16	38
14	60	50	30	30	15	12–16	58
15	60	50	30	48	16	20–25	56
16	60	50	30	60	12	30–35	60
17	60	50	30	18	15	5–8	51
18	70	50	30	30	15	15–18	49
19	70	50	30	18	15	8–18	56
20	60	30	50	30	15	10–15	22
21	60	30	50	30	15	12–15	58
22	60	60	20	30	15	10–15	56
23	60	60	20	42	18	18–21	58
24	60	60	20	72	15	35–40	68
25	60	70	10	30	15	10–15	33

When the cathode solution contains no alcohol the electrolysis is greatly effected by temperature, the more p-tolyl methyl ether being given the lower the temperature is (No. 1—No. 12). The concentration of the sulphuric acid should be maintained at about 60-70 %, for the more concentrated acid has the effect of resinising the aldehyde. The

greater current density gives the better yield. But when the current density becomes greater it is very difficult to regulate the temperature of the bath, which must always be kept low. In experiment from No. 13 to No. 25 it is seen that the presence of a certain amount of alcohol in the cathode solution favours the formation of p-tolyl methyl ether even at higher temperatures, and in consequence the current density can be made greater to increase the yield of the product. As was stated before, however, an excess of alcohol has quite the contrary effect (No. 20).

2. Salicylaldehyde

In the electrolytic reduction of salicylaldehyde hitherto conducted in an alcoholic sulphuric acid solution[1], neither the corresponding alcohol nor phenol was obtained. I was able, for the first time, to reduce the aldehyde to saligenin at the mercury cathode by using a neutral cathode solution[2]. It was now found that at the zinc amalgam cathode the aldehyde can be reduced to o-cresol in a sulphuric acid solution with about 66% yield. The electrolysis and also the treatment of the cathode solution after electrolysis were conducted in the same way as in the previous experiment, and o-cresol obtained was purified by distilling it under 20 mm.

Table II

No.	Catholyte			Current density amp./100 sq. cm.	Current quantity amp.-hour	Temperature °C	o-Cresol %
	Sulphuric acid		Alcohol cc				
	%	cc					
1	15	80	—	30	15	10–15	—
2	30	80	—	72	24	35–40	15
3	50	80	—	72	28	35–40	23
4	60	80	—	48	30	25–30	43
5	60	80	—	60	30	30–35	45
6	60	80	—	72	30	35–40	34
7	65	80	—	72	30	50–55	12
8	70	80	—	36	24	16–25	19
9	60	50	30	48	12	20–25	45
10	60	50	30	60	12	35–40	52
11	60	40	40	69	12	40–45	41
12	60	60	20	72	12	35–40	66

1 Law, loc. cit; Schepss, loc. cit.

2 These memoirs, **11**, 407 (1928)

pressure. The portion distilled off at 93°−94° was found to boil at 189°−190° at the ordinary pressure and to crystallize in needles. The results of analysis were:

0.2347 gm. substance gave 0.6637 g CO_2 and 0.1545 g H_2O,
C=77.13 %, H=7.36 %; Calc. C=77.78 %, H=7.41 %.

The relation between its yield and the conditions for electrolysis is shown in Table II.

From the table it is seen that the reduction must be conducted at 30°−40° using a cathode solution consisting of 60 % sulphuric acid. The effect of alcohol on the electrolysis is similar to that in the case of anisaldehyde.

3. p-Oxybenzaldehyde

Schepss[1] succeeded in reducing it to p-cresol with 41 % yield. Using the zinc amalgam cathode I obtained a far better result. The reduction-product was subjected to fractional distillation under the reduced pressure of 18 mm. and the portion coming off at 95°−100° was collected, and it was purified by again distilling. It boiled at 200°−202°, and gave the following results when analysed,

0.1837 gm. substance gave 0.5226 g CO_2 and 0.1215 g H_2O,
C=77.79 %, H=7.40 %; Calc. C=77.78 %, H=7.41 %.

The reduction of this aldehyde is badly effected by alcohol, so that the presence of alcohol in the cathode solution must always be avoided (see Table III).

Table III

No.	Catholyte		Current density	Current quantity	Temperature	p-Cresol
	60% sulphuric acid cc	Alcohol cc	amp./100 sq. cm.	amp.-hour	°C	%
1	40	40	72	12	38−42	14
2	50	30	48	12	23−26	20
3	60	20	72	12	35−40	27
4	80	—	72	24	35−40	58

1 Loc. cit.

4. Vanillin

Law[1] could obtain no reduction products by electrolyzing vanillin in an alcohoric sulphuric acid solution with the cathode of copper or nickel, while Schepss[2] obtained creosol with 28 % yield by using a cadmium cathode. I took a sulphuric acid solution containing no alcohol as the cathode solution, to which vanillin was added in suspension. The electrolysis was carried out with the zinc amalgam cathode, the cathode solution being vigorously agitated. Creosol isolated in the usual way was found to boil at 219°−221°.

0.1711 gm. substance gave 0.4345 g CO_2 and 0.1114 g H_2O,
C=69.26 %, H=7.28 %; Calc. C=69.56 %, H=7.25 %.

In the experiment, the results of which are shown in the next table, 80 cc. of sulphuric acid of different concentrations was used in each case.

Table IV

No.	Sulphuric acid %	Current density amp./100 sq. cm.	Current quantity amp. hour	Temperature °C	Creosol %
1	20	60	20	45−50	40
2	30	60	20	40−45	51
3	40	60	20	45−50	46
4	40	60	25	25−30	49
5	50	42	25	20−25	51
6	50	72	28	35−40	73
7	60	72	28	35−40	75
8	60	72	28	45−50	68

The influence of the concentration of sulphuric acid is, in this case, not so considerable, though 50−60 % acid gave the best result. Temperature also does not much influence the reduction-reaction; at the lower temperatures the material yield was increased but the current efficiency was greatly decreased.

To see the influence of alcohol on the reduction of vanillin 50 cc. of 60 % sulphuric acid mixed with 30 cc. of alcohol was taken as the cathode solution, and electrolysis was conducted at 8°−10° with a current

1 Loc. cit.
2 Loc. cit.

having the density of 24 amp./100 sq. cm. As there was produced no creosol, the electrolysis was repeated with less concenrated sulphuric acid (35 %), greater current density (72 amp./100 sq. cm.) and higher temperature (40°−42°). Though creosol was thus obtained, the yield was not more than 16.5 %. How greatly alcohol interferes the progress of reduction of vanillin will be clear, when this is compared with the results given in No. 2 or No. 3 of Table IV.

5. Piperonal

It was reported in the previous communication[1] that piperonal can be reduced to piperonyl alcohol with 90 % yield, when it is electrolyzed in a neutral solution with a mercury cathode. Now the complete reduction of the aldehyde was undertaken by electrolyzing it in a sulphuric acid solution with a cathode of zinc amalgam. The reduction-product was extracted with ether and purified by fractional distillation. The portion boiling at 193°−194° was collected and analysed.

0.1974 gm. substance gave 0.5082 g CO_2 and 0.1075 g H_2O,

C=70.21 %, H=6.09 %; Calc. C=70.59 %, H=5.88 %.

The yield was, in the best case, 55 %, while Schepss[2] obtained 33 % yield by using cadmium as the cathode.

In the reduction of piperonal the presence of alcohol was found favourable, as is seen in the following table:

Table V

No.	Catholyte: 60% sulphuric acid cc	Catholyte: Alcohol cc	Current density amp./100 sq. cm.	Current quantity amp.-hour	Temperature °C	Homobrenzcatechin methylene ether %
1	80	—	60	30	30−35	31
2	80	—	72	28	48−50	29
3	50	30	24	13	5−10	33
4	50	30	60	16	35−40	53
5	50	30	72	12	35−40	55
6	60	20	72	12	35−40	40
7	70	10	30	20	12−18	27

In conclusion, I desire to express my warm thanks to Professor M. Matsui for his constant interest and encouragement throughout the work.

1 G. Shima, these memoirs, **11**, 425 (1928).
2 Loc. cit.

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